July, 1988] © *1988 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, ***61***, *2547—2550 (1988)*

Synthesis of C_3 and C_4 Paraffins from Synthesis Gas with Hybrid Catalyst

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(Received December 24, 1987)

Hybrid catalysts composed of the physical mixture of methanol synthesis catalysts and Y-type zeolites gave C_3 and C_4 paraffins from synthesis gas at 2.1 MPa, with a selectivity higher than 70%. The product contained small methane and little aromatic hydrocarbons. The hydrid catalyst kept its activity and selectivity at almost constant level for 50 h. The yield of hydrocarbon was much higher than the level estimated from the thermodynamic equilibrium of methanol formation from synthesis gas. The yield of hydrocarbon increased monotonically with the increase in temperature while the carbon number distribution of the product shifted to lower side between 523 and 623 K. The production of hydrocarbon was accompanied by the nearly equal amount of CO_2.

Several attempts to make LPG (C_3 and C_4 paraffins) selectively from synthesis gas have been made by using catalysts such as a supported Fe–Mn–Cu,[1] a fused iron,[2] and a supported molybdenum.[3] However, since these catalysts are so-called Fischer–Tropsch catalysts their product distributions closely follow the Anderson–Schulz–Flory distribution law,[4] the selectivity of LPG is only about 33% at most and 18% of methane selectivity is inevitable.[4]

It has been reported that the synthesis gas reaction on a hybrid catalyst comprising physical mixtures of methanol synthesis catalysts and zeolites gives hydrocarbon mixtures whose composition are much different from those of a Fischer–Tropsch synthesis.[5–10] In the hybrid catalyst system, methanol formed on the methanol synthesis catalyst is successively converted in situ to hydrocarbons on the zeolite catalyst. We have already reported that on the hybrid catalyst composed of a Cu–Zn mixed oxide catalyst and H-ZSM-5 or DAY (dealuminated Y-type zeolite), aliphatic paraffins with 3—6 carbon atoms were predominantly produced from synthesis gas with a low methane selectivity,[10] while the hybrid catalyst composed of a Pd/SiO_2 and H-ZSM-5 or mordenite gave aromatic hydrocarbons with high selectivity.[8]

This study focused on developing hybrid catalysts which make C_3 and C_4 hydrocarbons selectively and clarifying the effects of several operating factors which control the product selectivity.

Experimental

The methanol synthesis catalyst, Cu–Zn (H) was prepared according to the method described by Shimomura et al.[11] The catalysts composition was Cu:40, Zn:23, Al:27 (atm%). Cu-Zn (C) was commercially available one (BASF S8-45). Dealuminated Y-type zeolite (DAY) was supplied by Shokubai Kasei Co. REY was obtained by calcining Linde type SK-500 in air at 723 K for 3 h. Pt-Y was prepared from SK-40 by ion exchanging with aqueous ammonium hexachloroplatiniate and the loading was 0.1 wt%. Some of the physical properties of the zeolites are shown in Table 1.

The hybrid catalysts were prepared as follows: Equal weights of methanol synthesis catalyst and zeolite were physically mixed and were powdered under 100 mesh. Then, they were pressed to a disk and were finally crushed to granules with 20/40 mesh. About 2.0 g of the hybrid catalyst was placed in a tubular reactor with a 6 mm inner diameter and was activated in a hydrogen flow at 723 K.

A pressurized, flow-type reaction apparatus was used for the synthesis gas reaction.[6]

Results and Discussion

Synthesis of Hydrocarbons with a Variety of Hybrid Catalysts. Table 2 shows the catalytic properties of a variety of hybrid catalyst prepared by combining Pd/SiO_2, Cu-Zn(H), and Cu-Zn(C) with Y-type zeolite and ZSM-5. It is clear from the data that any Y-type zeolite exhibited an excellent LPG selectivity of C_3 and C_4 hydrocarbons, while the activity itself was strongly influenced by the methanol synthesis catalyst. ZSM gave a small amount of aromatic hydrocarbons which was mainly composed of tri- and tetramethylbenzenes.

The high selectivity of LPG fraction on the Y-type zeolite system should be attributed to the quick

Table 1. Physical Properties of Zeolites Used for Preparing Hybrid Catalyst

Zeolite	SiO_2/Al_2O_3 mole ratio	Pore size	Content of Al_2O_3	Acidity
		Å	mmol g^{-1}	meq. g^{-1}
H-ZSM-5	50.2	6	1.2	1.74
DAY	7.6	13	3.6	4.22
REY	4.9	13	4.5	4.31
PtY	4.8	13	5.0	4.55

Table 2. Synthesis Gas Conversion on Hybrid Catalysts

Methanol cat.	Cu-Zn(H)				Cu-Zn(C)
Zeolite	DAY	RE-Y	Pt-Y	ZSM-5	DAY
Product yield (carbon %)					
Hydrocarbons	15.9	17.6	19.6	17.0	35.7
Oxygenates	1.5	1.2	0.2	0.6	5.3
CO_2	14.7	16.6	16.4	16.2	30.7
Coke	0.4	—	—	—	—
Hydrocarbon distribution (carbon %)					
Aliphatics					
C_1	3.2	1.4	0.9	7.7	3.2
C_2	8.5	11.8	14.8	13.5	10.7
C_3	17.8	18.0	22.0	26.9	24.7
C_4	49.4	48.3	42.8	12.7	49.6
C_5	12.6	12.4	12.7	9.1	8.2
C_6^+	8.5	9.0	6.8	26.4	3.7
Aromatics	0	tr.	0	3.8	tr.

Methanol catalyst/zeolite: 1/1 (weight ratio), temperature: 573 K, pressure: 2.06 MPa, H_2/CO: 2/1 (mole ratio), W/F: 3.4 g-cat h mol^{-1}.

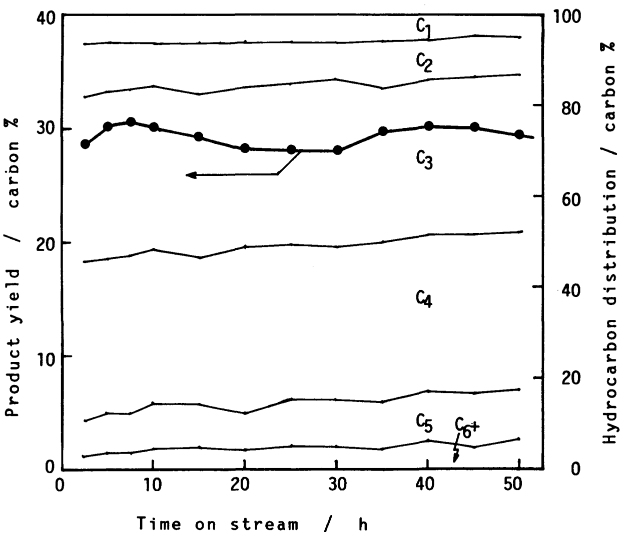

Fig. 1. Durability of hybrid catalyst: Cu-Zn(H)+DAY (1/1 by weight); Temperature 623+5 K; pressure 2.1 MPa; W/F=3.1 g-cat h mol^{-1}; $H_2/CO=2/1$ (mole ratio).

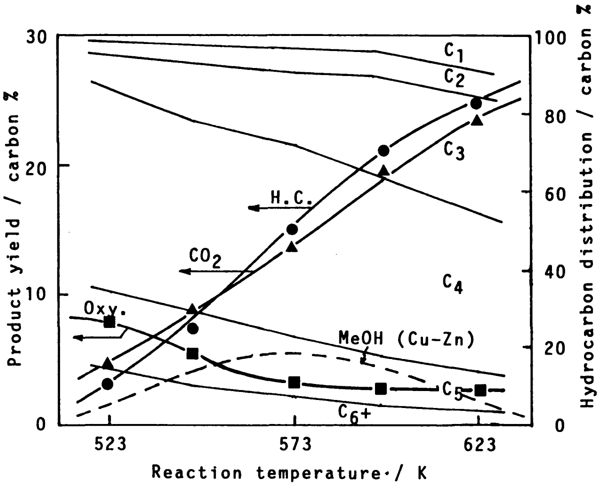

Fig. 2. Product yield and hydrocarbon distribution as a function of reaction temperature: Cu-Zn(H)+DAY (1/1 by weight); pressure 2.1 MPa; W/F=3.1 g-cat h mol^{-1}; $H_2/CO=2/1$ (mole ratio).

diffusion of olefins,which are the primary products of methanol conversion and their hydrogenation on the methanol synthesis catalyst.[10]

Durability of Hybrid Catalyst. Figure 1 shows the results of the synthesis gas reaction over a hybrid catalyst composed of Cu-Zn (H) and DAY. The catalytic activity was kept at almost a constant level over 50 hours, while a slight change in the hydrocarbon distribution occurred.

The level of synthesis gas conversion might be controlled by the activity of either catalyst of the hybrid catalyst, because the synthesis gas is first converted to methanol on the methanol synthesis catalyst and then the methanol is converted to hydrocarbons. Since the rate of synthesis gas conversion was substantially controlled by the rate of methanol formation in the present case, the constant activity of the present case should be attributed to the constant activity of the methanol synthesis catalyst. If the activity of DAY dropped quickly, which usually occur during the methanol conversion on the Y-type zeolite,[12] the product distribution should change quickly. The data in Fig. 1 indicate that the decrease in the zeolite activity was also quite slow. The slow deactivation of the zeolite should be attributed to the quick hydrogenation of olefins on the methanol synthesis catalyst,[8] which inhibits the polymerization of olefins to aromatics or coke.

Operational Factors Controlling Catalyst Activity and Product Selectivity. The catalytic activity and the product selectivity of the hybrid catalyst are influenced by several operational factors as demonstrated in figures through 2 to 5.

a. Temperature. As shown in Fig. 2, the hydro-

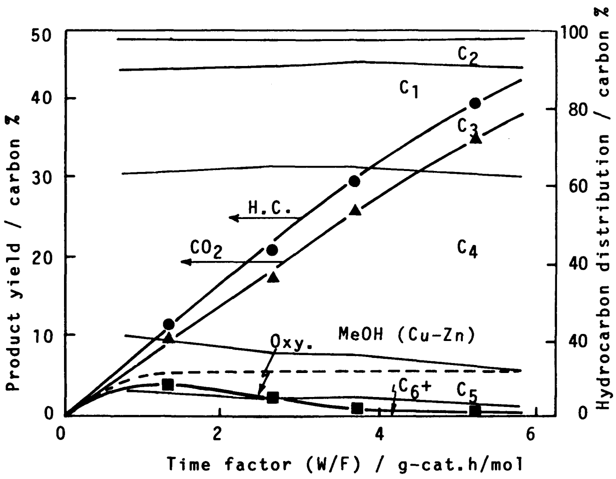

Fig. 3. Product yield and hydrocarbon distribution as a function of time factor: Cu-Zn(H)+DAY (1/1 by weight); temperature 623 K; pressure 2.1 MPa; $H_2/CO=2/1$ (mole ratio).

carbon yield increased monotonically and the yield of oxygenated compounds decreased with increasing reaction temperature while the product yield from the synthesis gas conversion on Cu-Zn(H) alone (broken line) reached a maximum level (ca. 5%) at approximately 573 K and then decreased due to the thermodynamic limitation of the methanol formation from synthesis gas. The high level of synthesis gas conversion on the hybrid catalyst could be attributed to the successive conversion of methanol to hydrocarbons on the zeolite as shown below.

$$2n\mathrm{CH_3OH} \rightleftarrows n\mathrm{CH_3OCH_3} \longrightarrow \mathrm{C}_n\mathrm{H}_m + n\mathrm{H_2O}$$

Product distribution is also strongly influenced by reaction temperature. At 573 K or lower, a significant amount of oxygenates (mostly dimethyl ether) was observed in the product suggesting the incomplete conversion of methanol to hydrocarbons on DAY at such low temperatures. The degree of carbon chain growth decreased monotonically with an increase in temperature. It is characteristic that the selectivity of C_4 paraffins was extraordinarily high and reached a maximum as high as 50% at 573 K. Among C_4 paraffins, the fraction of isobutane was about 3 times higher than that of normal butane. This value is much higher than that of the butane mixture in thermodynamic equilibrium. The reason is not clear yet.

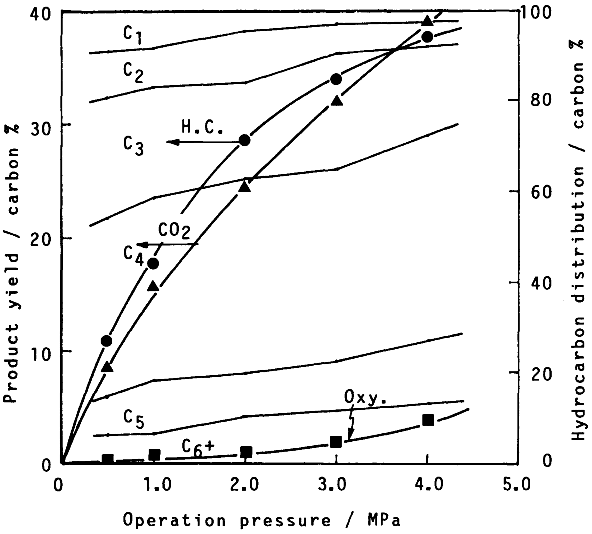

Fig. 4. Product yield and hydrocarbon distribution as a function of time factor: Cu-Zn(H)+DAY (1/1 by weight); temperature 623 K; W/F=3.1 g-cat h mol^{-1}; $H_2/CO=2/1$ (mole ratio).

b. Contact Time. The hydrocarbon yield was almost proportional to the contact time (W/F) as shown in Fig. 3, while methanol yield on the Cu-Zn(H) catalyst was independent of the time factor (dotted line). It suggests that products such as light paraffins or carbon dioxide have little suppressive effect on either methanol formation or methanol conversion to hydrocarbons. Also, the hydrocarbon distribution was never affected by the contact time, which suggests that apparently no significant secondary reactions of product hydrocarbon took place.

c. Reaction Pressure. Figure 4 shows how the reaction pressure affects the synthesis gas conversion on the hybrid catalyst. The hydrocarbon yield increased monotonically with an increase in the pressure, however, the promotional effect of pressure on this catalyst is not as remarkable as that on the Pd/SiO_2 based catalyst.[8] A slight increase in the hydrocarbon formation and a marked increase in the oxygenated formation above 3 MPa could be attributed to the relative rate of methanol formation and its conversion. The increase in the reaction pressure contributes only to the increase in the methanol formation. However, since the rate-determining step on this hybrid catalyst (Cu-Zn(H)/DAY=1/1 by weight) is the conversion of methanol to hydrocarbon,[12] the increase in methanol formation should have little effect on hydrocarbon formation but it should contribute to the increase in the oxygenates formation.

d. Composition of Synthesis Gas. The composition of synthesis gas (H_2/CO ratio) exhibited a complicated effect on the product yield and selectivity (Fig. 5). The hydrocarbon yield was in the similar level between $H_2/CO=3/1$, and 2/1 and then decreased markelly with decreased H_2/CO ratio, while that of oxygenates decreased drastically when the H_2/CO ratio in the feed was decreased from 3/1 to 1/1.

These phenomena are explained as follows: in principle, the rate of methanol formation is proportional to the partial pressure of hydrogen,[13] and thus the product yield should be higher at high H_2/CO ratios. The hydrocarbon yield at $H_2/CO=3/1$, however, was in the same level to that at $H_2/CO=2/1$.

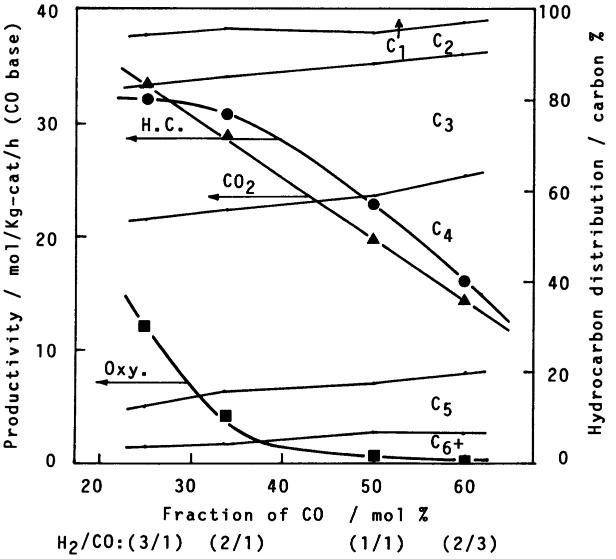

Fig. 5. Space time yield of each product and hydrocarbon distribution as a function of feed gas composition: Cu-Zn(H)+DAY (1/1 by weight); temperature 623 K; pressure 2.1 MPa; W/F=3.1.

The phenomena can be attributed to the fact that the rate-determining step of the present hybrid catalyst, where the hybrid catalyst is composed of equal weights of Cu-Zn(H) and DAY, is the methanol conversion step. Thus, the high H_2/CO ratio contributes only to the increase in the methanol (and DME) concentration in the catalyst bed. In fact, the yield of DME was much higher with the feed gas at $H_2/CO=3/1$. On the other hand, when the H_2/CO ratio is 1/1 or lower the methanol formation should be the rate limiting and thus, the rate of hydrocarbon formation decreases with the decrease in the H_2/CO ratio. The idea is also supported by the fact that little oxygenates is formed when the H_2/CO ratio is 1/1 or lower.

Conclusion

It has been confirmed that the hybrid catalysts composed of Cu-Zn mixed oxide methanol synthesis catalyst and Y-type zeolite exhibits a highly active, selective and stable catalysis for making LPG from synthesis gas. The catalytic activity is substantially controlled by the activity of the methanol synthesis catalyst. Other catalytic properties such as the product selectivity, the temperature characteristic, the pressure characteristic are explained in terms of the relative rate of methanol synthesis and its conversion to hydrocarbons.

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