

Synthesis Gas Conversion Utilizing Mixed Catalyst Composed of CO Reducing Catalyst and Solid Acid

IV. Selective Synthesis of C₂, C₃, and C₄ Paraffins from Synthesis Gas

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It was found that synthesis gas was converted selectively to C₂-C₄ paraffins with hybrid catalysts composed of a physically mixed methanol synthesis catalyst (Pd/SiO₂) and Y-type zeolites. The favorable conditions were 300-350°C and 1.0-5.1 MPa. A hybrid catalyst which contained a steam-treated high-silica Y-zeolite gave C₂-C₄ paraffins with the selectivity higher than 85% with an almost complete lack in aromatic hydrocarbons and coke with a methane selectivity of 2% or less, while methanol conversion on the zeolite gave aromatic hydrocarbons and coke with selectivities of 30 and 11%, respectively. The chain growth probability of the hydrocarbon, α_n which has been determined by ratio of the sum of C_{n+1}⁺ hydrocarbons to the sum of C_n⁺ hydrocarbons decreased with increasing carbon number from 0.99 (C₁) to 0.20 (C₅). © 1985 Academic Press, Inc.

INTRODUCTION

Several attempts have been made for developing new catalysts which produce C₂-C₄ hydrocarbons from synthesis gas. Kodama *et al.* have developed Fe-Mn-Cu catalysts (1, 2). Hoogendoorn at SASOL has demonstrated that a fused iron catalyst is effective for producing C₁-C₄ hydrocarbons (3). Recently, Murchison at Dow Chemical Company has claimed that supported molybdenum catalysts modified with potassium ion are active and stable catalysts for producing light hydrocarbons even in the presence of hydrogen sulfide (4).

However, these catalysts are not selective enough from the standpoint of the production of C₂-C₄ hydrocarbons. Especially, the formation of methane with fairly high selectivity poses a serious problem because of its hard separability from unconverted synthesis gas. Since the above-mentioned catalysts belong to the category of Fischer-Tropsch catalyst, the distribution of product hydrocarbon on these catalysts follows the Schulz-Flory distribution, which pre-

dicts the coproduction of methane with a fairly high selectivity being inevitable (5).

The present authors showed that the synthesis gas conversion with hybrid catalysts prepared by physically mixing a methanol synthesis catalyst and modified mordenites or H-ZSM-5 gave lower paraffins and aromatic hydrocarbons from synthesis gas under fairly low pressure (ca. 2.1 MPa) and higher temperature (623 K) with the yield which exceeded the thermodynamic limit of methanol formation from synthesis gas (5-7). This implies the fast conversion of methanol, the primary product, on zeolite via dimethyl ether to hydrocarbons. Along with the hydrocarbon products on the hybrid catalysts the paraffins were mostly methane, ethane, and propane, and the aromatic hydrocarbons were tetra-, penta-, and hexamethyl benzenes. The former were possibly produced by catalytic hydrogenation of lower olefins on the methanol synthesis catalyst, and the latter by the successive methylation of product toluene or xylene with methanol on the zeolite, respectively (6).

The present work has aimed at the selec-

TABLE 1
Physical Properties of Zeolites

| | SiO ₂ /Al ₂ O ₃ (mole ratio) | Acidity (meq/g) | Pore size ^a (Å) |
|---------|------------------------------------------------------------------|--------------------|-------------------------------|
| H-M | 14.6 | 1.74 | 6.9 |
| H-ZSM-5 | 50.2 | 3.74 | 6.0 |
| AW-500 | 10.0 | — | 4.0 |
| H-Y | 4.8 | 4.63 | 13.0 |
| DAY | 7.6 | 4.22 | 13.0 |
| S-DAY | 7.6 | 2.26 | 13.0 |

^a Data from Ref. (8).

tive synthesis of C₂, C₃, and C₄ hydrocarbons from synthesis gas with hybrid catalysts composed of methanol synthesis catalyst (Pd/SiO₂) and Y-type zeolites.

EXPERIMENTAL

Catalysts were prepared by mixing equal weight amounts of fine powdery (<100 mesh) methanol synthesis catalysts and zeolite and then molding the mixture under pressure. Methanol synthesis catalyst was 4 wt% Pd on SiO₂ (Pd/SiO₂). It was prepared by impregnating a commercially available silica gel (Fuji Davison. ID gel) with PdCl₂ from its acidic aqueous solution and then by reducing the precursor in flowing hydrogen at 673 K for 2 h. Details of the catalyst preparation have been described in the preceding paper (6). The dispersion of palladium, measured by CO chemisorption, was 14%.

Zeolites used were H-Y prepared from Na-Y (Linde SK-40), commercially available. An A-type zeolite (Linde AW-500), a high-silica Y-type zeolite (DAY) which was supplied by Shokubai Kasei Inc., a steam-treated DAY (S-DAY), a commercially available H-Mordenite (H-M, Norton 100H), a commercially available and home-made H-ZSM-5. S-DAY was prepared by treating DAY with flowing steam at 723 K for 3 h and then with nitrogen gas at the same temperature for 1 h. H-ZSM was prepared following the method described in U.S. Patent 3,702,886. All zeolites were

calcined at 773 K for 3 h before combining with Pd/SiO₂. Zeolites were selected mainly based on their pore size. The values of SiO₂/Al₂O₃ ratio, the acidity which is determined by NH₃ chemisorption and the effective pore diameters of zeolites used are shown in Table 1. TPD spectra of adsorbed NH₃ from zeolites were determined following the method which has been described elsewhere (9).

Synthesis gas reactions were conducted using a pressurized fixed-bed flow type reaction apparatus with a bubbler reactor of 6-mm inner diameter. Details of the reaction procedures and the product analysis have been described elsewhere (6).

RESULTS AND DISCUSSION

Conversion of Synthesis Gas with Pd/SiO₂-Zeolites Catalysts

The data in Table 2, which have been obtained by the reaction of synthesis gas over hybrid catalysts containing Pd/SiO₂ as the methanol synthesis catalyst, show that not only the yield but also the distribution of product hydrocarbons are strongly influenced by the zeolites employed. It is clear that on catalysts containing ZSM-5 or high-silica mordenite aromatic hydrocarbons are formed as well as aliphatic hydrocarbons composed of mainly C₁-to-C₃ paraffins while the catalysts containing Y-type zeolites or AW-500, little aromatic hydrocarbons are formed but lower paraffins with 1 to 4 carbon atoms are produced. It is interesting to note that the main products on the catalysts containing Y-type zeolite are C₂-C₄ paraffins and the ratio of iso-C₄ to n-C₄ is rather close to one whereas the products with the AW-500-based catalyst are mostly C₁-C₃ paraffins and the i/n ratio of C₄ hydrocarbons is close to zero. It should be also noted that little aliphatic olefins were formed from synthesis gas (not shown in Table 2) whereas the conversion of methanol on zeolites such as H-ZSM-5, AW-500, and DAY (7) gave olefins with high selectivities. This is attributable to the hydroge-

TABLE 2
Hydrogenation of CO on Hybrid Catalysts Containing Pd/SiO₂

| | Zeolite | | | | | |
|------------------------------------|-----------------------------------------------|---------|--------|------|------|-------|
| | H-M | H-ZSM-5 | AW-500 | H-Y | DAY | S-DAY |
| | Product yield (%/CO fed) | | | | | |
| Hydrocarbon | 8.0 | 10.8 | 7.3 | 6.5 | 14.6 | 12.7 |
| Oxygenates | tr. | tr. | tr. | tr. | tr. | tr. |
| CO ₂ | 3.3 | 5.6 | 3.4 | 2.7 | 5.9 | 10.0 |
| | Hydrocarbon distribution (wt% in carbon base) | | | | | |
| Aliphatics | | | | | | |
| C ₁ | 12.6 | 6.8 | 13.8 | 12.6 | 16.3 | 5.0 |
| C ₂ | 39.9 | 19.8 | 30.3 | 22.3 | 18.2 | 17.0 |
| C ₃ | 24.8 | 30.4 | 36.1 | 21.2 | 32.8 | 41.6 |
| C ₄ | 5.3 | 4.8 | 12.8 | 21.7 | 22.2 | 26.3 |
| C ₅ | 2.2 | 2.0 | 1.9 | 9.3 | 8.0 | 8.0 |
| C ₆ ⁺ | 4.2 | 2.8 | 1.9 | 4.9 | 1.5 | 2.1 |
| Aromatics | 10.7 | 33.4 | 0 | tr. | 0.9 | 0 |
| Coke | — | — | — | — | — | 0.6 |
| i-C ₄ /n-C ₄ | 0.9 | 0.2 | 0.1 | 1.1 | 0.7 | 0.7 |

Note: Pd/SiO₂: zeolite = 1:1 (weight ratio), temperature = 623 K, pressure = 2.06 MPa, H₂/CO = 2/1 (mole ratio), W/F = 10 g-cat h/mol.

nation of olefins by methanol synthesis catalysts. As demonstrated in Table 4 ethylene and propylene incorporated in the synthesis gas were hydrogenated almost completely to the corresponding paraffins under conditions for methanol synthesis.

It is reasonable that with catalysts containing H-M or H-ZSM-5, which give aromatic hydrocarbon upon methanol conversion, polymethyl benzenes are formed with fairly high selectivity as indicated in the preceding paper (6). It is also reasonable that only aliphatic paraffins are formed with the catalyst containing AW-500. Because its small pores do not allow the formation of not only aromatic hydrocarbons but also even isobutane from methanol.

However, in the conversion of methanol to hydrocarbons, large-pore zeolites give polymethyl benzenes (mainly hexamethyl benzene) and coke with high selectivity as demonstrated by Anderson *et al.* (9) and by our own work (Table 3). This is in sharp contrast with the fact that the synthesis gas reaction over hybrid catalysts containing

Y-type zeolites give little aromatic hydrocarbons and coke (whose selectivity is 0.6% for S-DAY-based catalysts). The phenomenon is explained as follows: although Y-type zeolites have pores which are large enough to allow the formation of methyl benzenes, even hexamethyl benzene, lower olefins which are the intermediates from methanol to aromatic hydrocarbons diffuse quickly within the pores because of their large size and come out of pores into bulk gas phase. Olefins in the gas phase would be easily hydrogenated on the Pd/SiO₂ catalyst by hydrogen contained in the synthesis gas as demonstrated in Table 4. The details of the process will be discussed in the next chapter.

The synthesis gas reaction on the DAY-based catalyst is characterized by the hydrocarbon yield which is twice or more higher than that of H-Y-based catalyst while the hydrocarbon distribution is quite similar to each other. However, the reason for this is not clear yet. In the case of the S-DAY-based catalyst hydrocarbon distribu-

TABLE 3

Conversion of Methanol on S-DAY Zeolite

| Catalyst | S-DAY | Pt-S-DAY ^b | Pt-S-DAY |
|-----------------------------------------------|----------------|-----------------------|----------------------|
| Balance gas | H ₂ | H ₂ | 2H ₂ + CO |
| Process time (h) | 4.5 | 4 | 4 |
| Conversion of MeOH (%) | 97.9 | 100 | 100 |
| Hydrocarbon distribution (wt% in carbon base) | | | |
| Aliphatic | | | |
| C ₁ | 6.9 | 57.8 | 8.9 |
| C ₂ | 8.2 | 6.1 | 18.2 |
| C ₂ ' | 4.6 | n.d. | tr. |
| C ₃ | 4.6 | 17.1 | 19.7 |
| C ₃ ' | 8.6 | n.d. | tr. |
| i-C ₄ | 12.7 | 6.9 | 5.2 |
| n-C ₄ | 4.4 | 6.2 | 30.8 |
| C ₄ ' | 0.3 | n.d. | tr. |
| C ₅ | 9.9 | 4.7 | 12.3 |
| C ₆ | 6.6 | 1.1 | 1.7 |
| Aromatic | | | |
| C ₇ | 0.1 | tr. | tr. |
| C ₈ | 0.9 | | |
| C ₉ | 2.2 | | |
| C ₁₀ | 4.6 | | |
| C ₁₁ | 9.8 | | |
| C ₁₂ | 9.3 | | |
| C ₁₃ ⁺ | 0.3 | | |
| Coke | 7.0 | — | — |
| i-C ₄ /n-C ₄ | 2.8 | 1.1 | 5.9 |

Note. Catalyst S-DAY, temperature = 623 K, pressure = 1.47 MPa, W/F = 5.2 g-cat h/mol, P_{MeOH}: 0.015 MPa.

^a Average of 15 h of run.

^b Pt 0.5 wt%.

tion is markedly different from that of the DAY-based catalyst while the product yield is kept at the same level. That is, the selectivity of methane decreases from 16.3 to 5.0% (when the methane formation on Pd/SiO₂ is corrected, their values are 12.4 and 1.4%, respectively) and that of propane increases from 32.8 to 41.6%, respectively, while the selectivities of other products are rather constant. It means that the chain growth of carbon-carbon bond is more prominent for S-DAY.

Acid Characters of Y-Type Zeolite

The acid characters, which are deter-

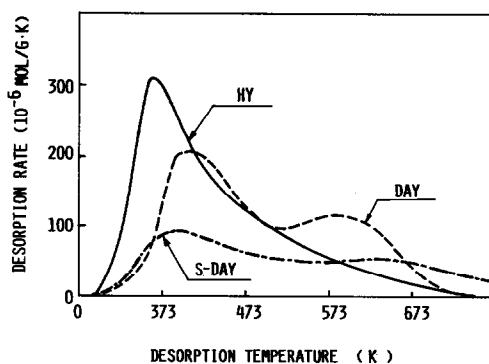


Fig. 1. TPD spectra of ammonia from H-Y, DAY, and S-DAY. Heating rate 6.7 K/min. Desorbed ammonia was measured with a mass spectrometer. Ammonia adsorption: H-Y, 4.63 mmol/g; DAY, 4.22 mmol/g; S-DAY, 2.26 mmol/g.

mined by TPD of chemisorbed NH₃ indicate, as illustrated in Fig. 1, that the acid of DAY is stronger than that of H-Y whereas the acid amount is smaller than that of H-Y. TPD spectrum of DAY is also characterized by its twin peaks which locate at around 400 and at 600 K. The authors have indicated that the latter peak is essential for the aromatics formation (11). In the case of synthesis gas conversion, however, the strong acid site might be effective in promoting methanol to hydrocarbons, especially for carbon chain growth.

TABLE 4

Conversion of Synthesis Gas in the Presence of Olefins^a

| Additives | Product yield (% carbon base) | | |
|----------------------------------|-------------------------------|-----------------------|------------------------|
| | — | Ethylene ^b | Propylene ^c |
| CH ₃ OH | 0.83 | 0.80 | 0.80 |
| CH ₃ OCH ₃ | 0.33 | 0.31 | 0.20 |
| CO ₂ | 1.0 | 0.98 | 0.95 |
| CH ₄ | 1.05 | 1.24 | 1.33 |
| C ₂ H ₄ | n.d. | 0.01 | n.d. |
| C ₂ H ₆ | 0.05 | 0.92 | 0.05 |
| C ₃ H ₆ | n.d. | n.d. | 0.01 |
| C ₃ H ₈ | n.d. | n.d. | 1.45 |

^a Catalyst = 4 wt% Pd/SiO₂, temperature = 623 K, pressure = 2.01 MPa, W/F = 5 g-cat h/mol.

^b C₂H₄/CO in feed gas was 0.51 × 10⁻² (mole ratio).

^c C₃H₆/CO in feed gas was 0.52 × 10⁻² (mole ratio).

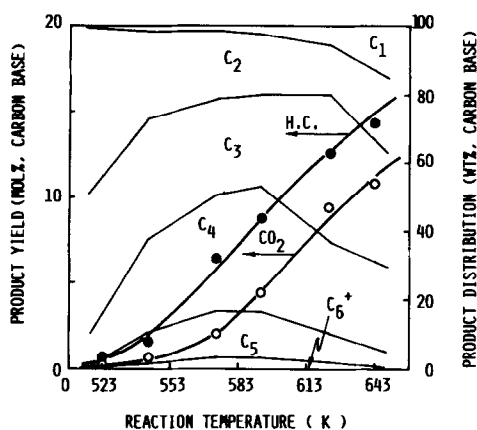


FIG. 2. Temperature effect on synthesis gas conversion with a hybrid catalyst. Pd/SiO₂:S-DAY = 1:1, 2.06 MPa, H₂/CO = 2/1, W/F = 10 g-cat h/mol.

The amount of chemisorbed NH₃ is smaller and its TPD spectrum is flat for S-DAY rather than DAY. However, it should be noted that a noticeable amount of NH₃ desorbs even above 700 K, which indicates that very strong acid is formed by steaming which might cause the enhanced chain growth. The details will be reported in a subsequent paper.

Operational Factors which Affect Activity and Selectivity

Temperature. Temperature exercises predominant effects on both activity and selectivity (Fig. 2). Hydrocarbon yield increases monotonously with increasing temperature, as in the case of a Pd/SiO₂-H-ZSM-5 catalyst (6) which covers a range from 523 to 643 K to reach 14% (carbon base) at 643 K while methanol yield from synthesis gas with the Pd/SiO₂ catalyst along with the gas reaches the maximum level (ca. 5%) at around 573 K and then decreases with the temperature to reach 1.2% at 623 K (6). This is attributed to the successive conversion of methanol to hydrocarbons.

Product distribution is also strongly influenced by reaction temperature as demonstrated in Fig. 3. Apparently, the degree of carbon chain growth is the highest at

around 593 K. Although methane selectivity is very low (1.1%) at 543 K, LPG (C₃ and C₄ hydrocarbons) selectivity is not high enough because of the high selectivity of ethane. The low level of the chain growth at lower temperature should be caused by the slow dehydrocondensation of methanol to hydrocarbons on zeolite. Above 527 K the degree of carbon chain growth decreases again, probably due to the decrease in adsorption equilibrium of olefins and to the increase in the rate of diffusion and hydrogenation of them. The high selectivity of methane is attributed to the methanation on the Pd/SiO₂ catalyst (6).

Time factor. Yield of hydrocarbons is proportional to time factor (*W/F*) as shown in Fig. 4. 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 hydrocarbon distribution is never affected by the time factor, suggesting that apparently no significant secondary reactions of hydrocarbon products take place. The above-mentioned assumption is reasonable considering that stable lower paraffins are formed at the early stage of reaction. No appearance of aromatic hydrocarbons, which occupy fairly large portions in the product from methanol conver-

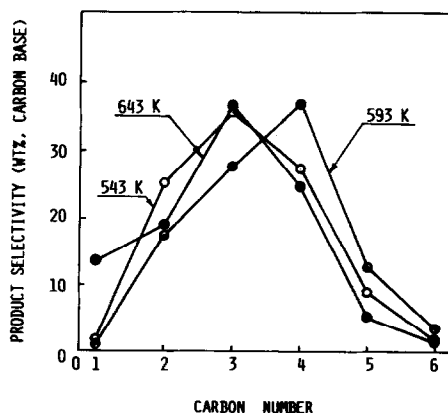


FIG. 3. Temperature effect on hydrocarbon distribution. Pd/SiO₂:S-DAY = 1:1, 2.06 MPa, H₂/CO = 2/1, W/F = 10 g-cat h/mol.

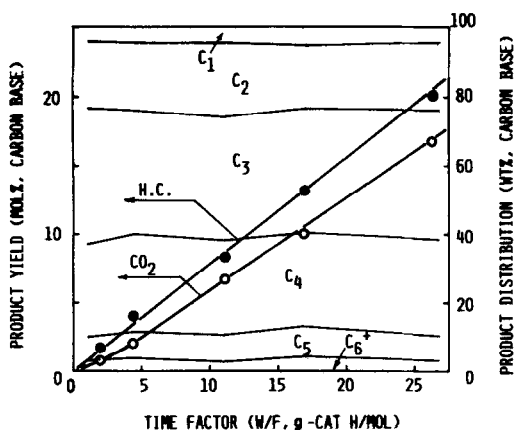


FIG. 4. Effect of time factor on synthesis gas conversion with a hybrid catalyst. Pd/SiO₂:S-DAY = 1/1, 623 K, 2.06 MPa, H₂/CO = 2/1.

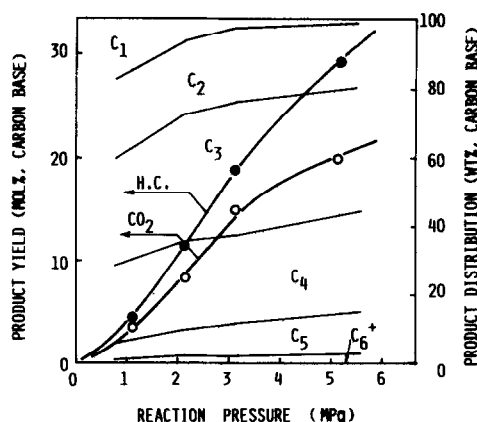


FIG. 5. Pressure effect on synthesis gas conversion with a hybrid catalyst. Pd/SiO₂:S-DAY = 1:1, 623 K, H₂/CO = 2/1, W/F = 10 g-cat h/mol.

sion on S-DAY, indicates that no aromatics are formed at any stage of the reaction in the present system. This is because the hydrogenolysis of aromatics on the Pd/SiO₂ catalyst (6) is not significant.

Pressure. Figure 5 shows that hydrocarbon yield is markedly accelerated by increasing reaction pressure while product pattern is not greatly affected except below 2.06 MPa. The acceleration of hydrocarbon formation with increasing reaction pressure should be attributed to the acceleration of methanol formation (12). The extremely low yields of methanol and dimethyl ether (<0.1%) at 623 K and under 2.06 MPa suggest that the rate of methanol formation is lower than that of methanol (or dimethyl ether) conversion to hydrocarbons under these conditions. On the other hand, the slight promotion of carbon chain growth by increased reaction pressure would be caused by the higher concentration of methanol (13) due to the higher rate of its formation. The selectivity of LPG reaches 66% accompanied by 1.5% of methane selectivity under 263 K and 5.1 MPa.

Reaction path and parameters controlling product pattern. It is clear from the data shown in the present study that the synthesis gas conversions on the hybrid catalyst containing Pd/SiO₂ and Y-type ze-

olite give little aromatic hydrocarbons while methanol conversion of Y-type zeolite alone gives a large amount of polymethyl benzenes. As already pointed out (6) the reaction net work for the hybrid system is expressed in Fig. 6. However, the difference between the former and the present case is that the zeolite is not H-ZSM-5- but Y-type zeolite with larger pores. The absence of aromatics in the product would be attributed to the instantaneous hydrogenation of olefins, which are intermediates from methanol to aromatic hydrocarbons, on the methanol synthesis catalyst. The Pd/SiO₂ methanol synthesis catalyst has been proven to be quite active for olefin hydrogenation under the present reaction conditions as demonstrated in Ta-

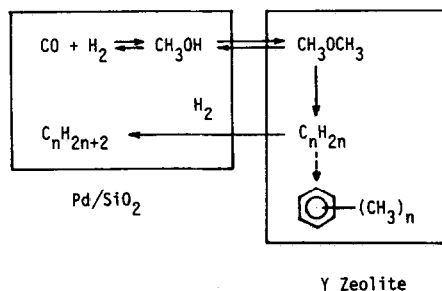


FIG. 6. Reaction scheme of CO hydrogenation on the hybrid catalyst composed of Pd/SiO₂ and Y-type zeolite.

TABLE 5
Chain Growth Probability of Hybrid Catalysts
Containing Pd/SiO₂

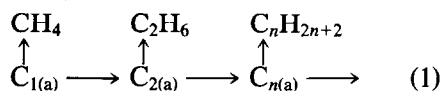
| | Zeolite | | | |
|-----------------|--------------------------|-------|-------|-------|
| | H-Y | S-DAY | S-DAY | S-DAY |
| Temperature (K) | 623 | 623 | 623 | 593 |
| Pressure (MPa) | 2.06 | 2.06 | 5.00 | 2.06 |
| | Chain growth probability | | | |
| α_1^a | 0.98 | 0.99 | 0.99 | 0.99 |
| α_2 | 0.74 | 0.82 | 0.81 | 0.82 |
| α_3 | 0.55 | 0.47 | 0.62 | 0.66 |
| α_4 | 0.40 | 0.28 | 0.34 | 0.31 |
| α_5 | 0.34 | 0.19 | 0.19 | 0.22 |

Note. Pd/SiO₂: zeolite = 1:1 (weight ratio), H₂/CO = 2/1 (mole ratio), W/F = 10 g-cat h/mol.

^a Corrected the methane formation on the Pd/SiO₂.

ble 4. The hydrogenation of olefins is most predominant in the catalyst system containing Y-type zeolite where the diffusion of olefins within zeolite is the fastest (14) and thus the residence time of olefins in the pores is the shortest because of its large pores. As it is clear from the data in Table 3 the methanol conversion on DAY containing 0.1% platinum under hydrogen or synthesis gas atmosphere give only aliphatic paraffins suggesting that hydrogenating ability of catalyst effectively inhibit the formation of aromatic hydrocarbons as well as coke deposition on zeolite. On the other hand aromatic hydrocarbons can be formed on hybrid catalyst containing H-ZSM-5 and H-M zeolites with middle-size pores which give enough space and residence time for the aromatics' formation.

Table 5 shows the chain growth probabilities calculated based on the product pattern demonstrated in Figs. 2 to 5, the reaction scheme shown in equation



and the definition in equation

$$\alpha_n = \frac{\text{C}_{n+1} + \text{product}}{\text{C}_n + \text{product}} \quad (2)$$

It has been well known that α values of Fischer-Tropsch synthesis are normally independent of carbon number of product hydrocarbon (15), which leads to the Schulz-Flory distribution. In the present case, however, α values decrease markedly with an increase in carbon number in all cases. Especially, it should be noted that α_1 value which determine the methane selectivity is close to 1.0 indicating that almost all of the C₁ species on zeolite participate in the chain growth. Other characteristic features of chain growth probability are summarized as follows. (1) Values of α on H-Y-based catalyst are rather close to each other compared to those of S-DAY-based catalyst, which indicates the hydrocarbon distribution is rather flat for the former catalyst. (2) On the S-DAY-based catalyst values of α_3 , α_4 , and α_5 increase with increasing pressure and decreasing temperature while α_1 and α_2 values are scarcely affected by reaction conditions.

Since the active species of chain growth on zeolite is supposed to be alkyl carbonium ion (16), they would desorb into the gas phase in two ways: as olefins leaving a proton on the zeolite and as paraffins with the capture of hydride ion from the zeolite surface or from other hydrocarbons. Since the stability of carbonium ion on zeolite has been known to be lower for lower carbonium ion, the probability of desorption should be higher for lower carbonium ion which leads the increased chain growth probability with increased carbon number if the first path is the main route of the product formation. However, this does not agree with the experimental data. On the other hand, the second route should be also favored for lower carbonium ions because of their higher reactivity. However, the source of hydride ion, which is generally the precursor of aromatic hydrocarbons or coke, is missing in the present case because neither aromatic hydrocarbons nor coke are formed.

Possible hydrogen source for the hydrogenation of alkyl carbonium ion is the hy-

drogen on zeolite which is spilled over from the Pd/SiO₂. However, there has been little information concerning the spillover phenomenon of hydrogen between solid particles and thus further studies are necessary to discuss with the subject in detail.

Another explanation for the data in Table 5 is that the reactivity of alkyl carbonium ion toward C₁ building block is higher for lower alkyl carbonium ion. But the idea has never been proven experimentally and thus also requires further study.

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