

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

### II. Direct Synthesis of Aromatic Hydrocarbons from Synthesis Gas

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The synthesis of aromatic hydrocarbons from carbon monoxide and hydrogen was studied under pressurized conditions using hybrid catalysts composed of a methanol synthesis catalyst (Pd/SiO<sub>2</sub>) and zeolites. Combination of Pd/SiO<sub>2</sub> with H-ZSM-5 or H-mordenite gave aromatic hydrocarbons with selectivities higher than 50%. Coupling of Pd/SiO<sub>2</sub> with H-Y gave little aromatics. Aromatic hydrocarbons formed on the H-ZSM-5 based catalyst, were mostly tetramethyl and pentamethyl benzenes, significantly different from those obtained by the reaction of methanol on the H-ZSM-5 alone. The yield of hydrocarbons was far higher than the level which is estimated from the thermodynamic equilibrium of methanol formation. The hydrocarbon formation was favored by the high reaction temperature and the high operating pressure. A reaction scheme of the hydrocarbon formation on the hybrid catalyst will be described which includes (i) formation of methanol, (ii) conversion of methanol to olefins, (iii) aromatization of olefins, (iv) hydrogenation of olefins on Pd/SiO<sub>2</sub>, and (v) methylation of aromatic hydrocarbons by methanol on zeolites.

#### INTRODUCTION

Synthesis of hydrocarbons from carbon monoxide and hydrogen (Fischer-Tropsch Synthesis) has been known since 1923. The process has been in commercial practice in South Africa (1). The product of Fischer-Tropsch synthesis is composed mostly of straight-chain aliphatic hydrocarbons with little aromatic hydrocarbons (2). Thus, the middle distillate fraction is excellent as diesel or burner fuel. However, the octane number of naphtha is too low to be used as motor gasoline without being reformed for octane improvement (3).

In 1975, Mobil Oil Company researchers succeeded in converting methanol into high octane gasoline with an excellent yield by utilizing a new type zeolite (ZSM-5) catalyst (4-7). Characteristic features of the reaction are (5)

(i) Methanol is first converted to aliphatic olefins via dimethyl ether and then to aromatic hydrocarbons.

(ii) Yield of methane and C<sub>2</sub> hydrocarbons are very low.

(iii) The final product is a mixture of aliphatic hydrocarbon with 3 to 6 carbon atoms which is rich in iso-paraffins and benzene derivatives.

(iv) Most of the benzene derivatives formed are monomethyl, dimethyl, and trimethyl benzenes with small amounts of tetramethyl benzenes.

(v) The formation of aliphatic paraffins is attributed to the transfer hydrogenation of olefins by hydrogen supplied by other olefins through their aromatization. Since then much research has been done from the standpoints of both process development and mechanistic study (7-9).

Chang *et al.* have revealed that light paraffins and aromatic hydrocarbons were directly formed from synthesis gas on complex catalysts composed of methanol synthesis catalyst such as Zr oxide or Zn-Cr mixed oxide and protonated ZSM-5 under severe conditions (83 atm and 427°C)

(14). However, the conversion of synthesis gas was rather low (about 38% or less). Theoretically, the reaction of synthesis gas to hydrocarbon on the complex catalyst is free from the thermodynamic limitation of methanol formation because of the conversion of product methanol to hydrocarbons. Therefore the reaction might be performed at lower pressure and higher temperature than those employed for methanol synthesis.

The present authors have reported that aliphatic paraffins with 2 to 6 carbon atoms were selectively formed from synthesis gas with complex catalysts composed of Cu-Zn-Al mixed oxide (methanol synthesis catalyst) and H-Y or H-ZSM-5 zeolite at around 350°C and under 21 atm (15). Although the conversion of carbon monoxide was high (ca. 50%) even under low reaction pressures, the yield of aromatic hydrocarbons was quite low. The present authors have also tried to utilize the supported palladium catalyst, which have been known to have excellent activity for methanol formation from synthesis gas under both moderate and severe conditions (10), as one of the components and found that aromatic hydrocarbons are formed with a fairly high selectivity (16).

In the present work direct synthesis of aromatic hydrocarbons from synthesis gas with hybrid catalysts composed of Pd/SiO<sub>2</sub> and several zeolites under moderate conditions has been studied to clarify the factors which control the product selectivity.

#### EXPERIMENTAL

**Catalyst Preparation.** A Pd/SiO<sub>2</sub> catalyst (Pd 4 wt%) was prepared by impregnating a commercially available silica gel (Fuji Davison ID gel; specific surface area: 270 m<sup>2</sup>/g; pore volume: 1.1 cm<sup>3</sup>/g; mean pore diameter: 140 Å) with palladium chloride from its acidic aqueous solution by a dry-up method, followed by drying in an air oven at 323 K for 20 h. The catalyst precursor was activated by being reduced in flowing hydrogen at 673 K, for 2 h. The dispersion

of supported palladium metal was 14% (by CO chemisorption).

ZSM-5 zeolite was prepared following the method described in U.S. Patent 3,702,886. The mole ratio of SiO<sub>2</sub> to Al<sub>2</sub>O<sub>3</sub> in the zeolite was 67. Sodium ion in the zeolite were exchanged with protons by treating repeatedly with hydrochloric acid at around 340 K and calcining in air at 723 K for 3 h (H-Z). H-Y zeolite (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio: 11) was activated by calcining NH<sub>4</sub>-Y zeolite at 723 K for 3 h to remove ammonia. H-mordenite (H-M) zeolite was obtained by calcining a commercially available mordenite (Norton Zeolon 100 H) at 723 K.

Hybrid catalysts were prepared by physically mixing the powders (under 150 mesh) of Pd/SiO<sub>2</sub> and zeolites, then pressing the mixture into a disk and finally crushing it into granules (20–40 mesh).

**Reaction Apparatus and Procedure.** A pressurized flow-type reaction apparatus was used for the study. The apparatus was equipped with an electronic temperature controller for a furnace, a tubular reactor with an inner diameter of 10 mm, a flow regulator-controller, and a back-pressure regulator. Hydrogen and carbon monoxide were fed independently from cylinders and mixed at the inlet of the reactor. All products from the reactor were withdrawn at gaseous state and were analyzed by gas chromatography.

#### RESULT AND DISCUSSION

##### *Methanol Synthesis on Pd/SiO<sub>2</sub> Catalyst*

As can be seen in Fig. 1, the yield of methanol increases with increasing temperature to give a peak at about 573 K and then decreases sharply with increased temperature. The yield of methanol is only 0.9% at 623 K and under 2.06 MPa. The decrease in methanol yield above 300°C is attributed to thermodynamic limitation (14). This idea is supported by the fact that the yield of methanol is independent of the time factor ( $W/F$ ) between 0.5 and 20 g-cat · h/mol while the yield of methane and carbon dioxide is pro-

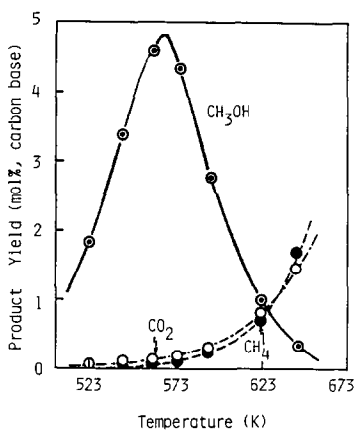


FIG. 1. Reaction of synthesis gas on a Pd-SiO<sub>2</sub> catalyst (1). Pd-SiO<sub>2</sub>, 4 wt%; H<sub>2</sub>/CO = 2/1; W/F = 4.5 g · h/mol; P = 2.06 MPa.

portional to the time factor (Fig. 2). This means that the equilibrium between synthesis gas and methanol is attained within a short residence time and that the rate of methanol formation is proportional to the amount of synthesis gas which passes over a unit weight of catalyst per unit time. For example, the rate of methanol formation is 6.0 mmol/g-cat · h at 623 K, at 0.5 g-cat · h/mol and under 212 KPa, which is two times larger than that of the highest value shown in Fig. 1. Thus, it is concluded that the catalytic activity of Pd/SiO<sub>2</sub> for methanol formation is very high at 623 K.

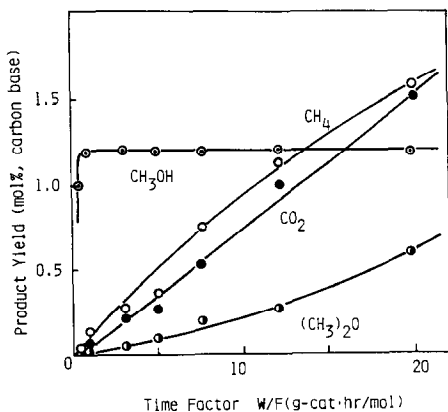


FIG. 2. Reaction of synthesis gas on a Pd-SiO<sub>2</sub> catalyst (2). Pd-SiO<sub>2</sub>, 4 wt%; H<sub>2</sub>/CO = 2/1; P = 2.06 MPa; Temp. = 623 K.

The major by-products are hydrocarbons, about 90% of which are methane and carbon dioxide. Although the amount of methane and carbon dioxide are quite small below 573 K, they become comparable to that of methanol at 623 K.

### Effect of Mixed Zeolites on the Conversion of Synthesis Gas and Product Selectivity

**Zeolite effect.** Results of synthesis gas conversion on hybrid catalysts composed of Pd/SiO<sub>2</sub> and H-Z, H-Y, or H-M are shown in Table I. It should be noted that by mixing zeolites with Pd/SiO<sub>2</sub>, the yield of oxygenates (mostly methanol and dimethyl ether) decreases to almost zero; whereas, the yield of hydrocarbons increases by about 1 order of magnitude. Among the zeolites, H-Z is most effective and H-Y is least effective as one component of the hybrid catalyst for converting synthesis gas

TABLE I

Results of Hydrocarbon Synthesis from Synthesis Gas with Hybrid Catalysts

Catalyst	H-Z <sup>a</sup>	Pd/SiO <sub>2</sub> + H-Z	Pd/SiO <sub>2</sub> + H-Y	Pd/SiO <sub>2</sub> + H-M
Temperature (K)	638	628	630	627
Yield (C-wt%)				
Hydrocarbons	97	11	9.8	8.3
Oxygenates	tr.	tr.	tr.	0.1
CO <sub>2</sub>	—	5.5	5.6	2.5
Hydrocarbon distribution (C-wt%)				
Aliphatic				
C <sub>1</sub>	0.5	7.5	5.3	9.2
C <sub>2</sub>	0.7	15.1	23.1	14.5
C <sub>3</sub>	13.7	30.8	34.9	11.2
C <sub>4</sub>	21.5	5.9	25.8	6.6
C <sub>5</sub>	11.6	2.4	8.3	2.7
C <sub>6</sub>	6.0	1.5	2.3	1.8
C <sub>7</sub>	1.6	0.3	0.3	1.7
C <sub>8</sub>	0.2	0.9	0.03	1.2
Total	55.8	64.4	99.96	48.8
Aromatic				
C <sub>6</sub>	1.0	—	—	—
C <sub>7</sub>	6.9	—	—	—
C <sub>8</sub>	14.1	—	—	0.4
C <sub>9</sub>	10.0	0.8	—	0.6
C <sub>10</sub>	11.8	20.4	—	1.7
C <sub>11</sub>	0.4	12.5	0.04	20.6
C <sub>12</sub>	tr.	2.0	—	22.2
C <sub>13</sub>	—	—	—	5.6
Total	44.2	35.7	0.04	51.2

Feed: Synthesis Gas (H<sub>2</sub>/CO = 2) Pressure: 2.06 MPa  
W/F = 8.8–8.9 g-cat · h/mol Mixing ratio of catalysts: (1 : 1)

<sup>a</sup> Feed: syngas/CH<sub>3</sub>OH = 9/1.

TABLE 2  
Olefin Content in C<sub>2</sub>-C<sub>4</sub> Products

Catalyst	H-ZSM-5	H-Y	Pd/SiO <sub>2</sub> + H-ZSM-5
Feed	CH <sub>3</sub> OH <sup>a</sup>	CH <sub>3</sub> OH <sup>a</sup>	H <sub>2</sub> + CO
Temperature (K)	638	605	628
Olefin content (%)			
C <sub>2</sub>	28.6	39	0.2
C <sub>3</sub>	2.9	77	0.2
C <sub>4</sub>	1.9	27	tr.

<sup>a</sup> Syngas/CH<sub>3</sub>OH = 9/1.

into hydrocarbons. However, the ability of each catalyst to form hydrocarbons is not much different.

Synthesis gas conversion on the hybrid catalyst is also characterized by the formation of carbon dioxide, which amounts to 50 to 60% of the hydrocarbons on the CO base. Carbon dioxide formation is not attributed to the disproportionation of carbon monoxide but to the CO shift reaction. This idea is supported by the facts that palladium metal has low CO decomposition activity (17) and that the amount of carbon deposited on the hybrid catalyst during the synthesis gas reaction is far less than the amount of carbon dioxide formed.

Distribution of product hydrocarbons, is significantly affected by the zeolite component. In the case of the H-Z based catalyst, the main products are aliphatic paraffins with 2 to 3 carbon atoms and methyl benzenes with 3 to 5 methyl groups. On the H-M based catalyst, C<sub>11</sub> and C<sub>12</sub> aromatic hydrocarbons are formed along with C<sub>1</sub>, C<sub>2</sub>, and C<sub>3</sub> paraffins. Aliphatic paraffins with 2 to 5 carbon atoms are selectively formed on the H-Y based catalyst.

It should be noted that the major aromatic hydrocarbons formed on the H-Z based catalyst are tetramethyl and pentamethyl benzenes, whereas the product of methanol conversion on H-Z alone under similar reaction condition is composed of mostly C<sub>3</sub><sup>+</sup> aliphatic hydrocarbons and aromatic hydrocarbons mostly composed of xylenes, trimethyl benzenes and tetra-

methyl benzenes, as shown in Table 1. Another marked characteristic of those two cases is that the olefin content in aliphatic hydrocarbons is fairly high for the case of methanol conversion while little aliphatic olefins are formed in the synthesis gas reaction (Table 2). This subject will be discussed afterward.

*Effects of catalyst composition.* In the present catalyst system both hydrocarbon yield and product distribution should be affected by the rates of methanol formation as well as its conversion. While the yield of hydrocarbons does not change so much with the change in the catalyst composition of the hybrid catalyst, the product pattern is effected significantly by the composition (Fig. 3). With decreasing Pd/SiO<sub>2</sub>, the content of aromatic hydrocarbons in the product, especially that of tetramethyl benzenes, increases sharply, which is accompanied by the decrease in the C<sub>1</sub> to C<sub>3</sub> paraffins. This suggests that the Pd/SiO<sub>2</sub> acts not only as a catalyst for methanol formation but also suppresses the formation of aromatic hydrocarbons.

The effect of mixing zeolites with a Pd/SiO<sub>2</sub> catalyst is summarized: (i) The product yield increases almost by 1 order of magnitude at 723 K. (ii) One of the main

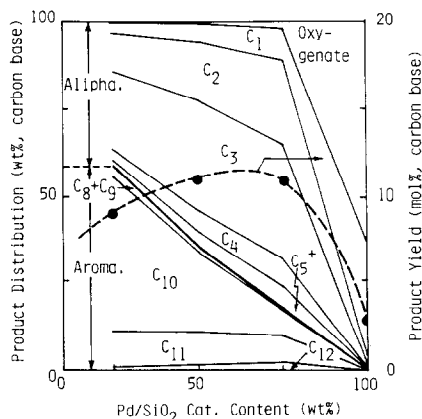


FIG. 3. Effect of catalyst composition on the synthesis gas reaction over a hybrid catalyst. Pd-SiO<sub>2</sub> plus H-Z; H<sub>2</sub>/CO = 2/1; P = 2.06 MPa; Temp. = 623 K; W/F = 9 g · h/mol.

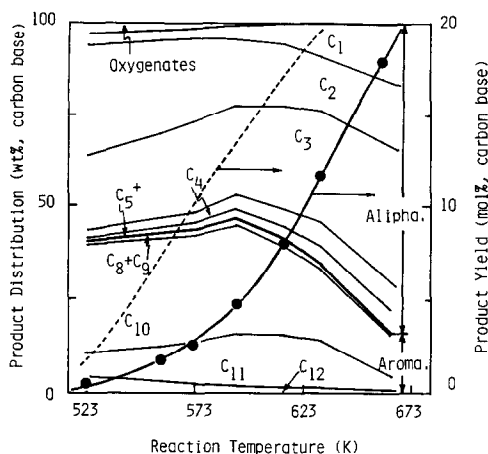


FIG. 4. Temperature effect on the synthesis gas reaction over a hybrid catalyst. Pd-SiO<sub>2</sub>/H-Z = 1/1 (weight ratio); H<sub>2</sub>/CO = 2/1; P = 2.06 MPa; W/F = 9 g · h/mol.

products is ethane whose yield is quite low when methanol is reacted only on zeolite. (iii) The Pd/SiO<sub>2</sub> catalyst shows a strong negative effect on the formation of aromatics. (iv) Aromatic hydrocarbons are more highly methylated on the hybrid catalyst than on H-Z only.

*Effects of operational factors.* Contrary to the reaction on the Pd/SiO<sub>2</sub> catalyst alone (Fig. 1) the yield of products on the hybrid catalyst increase monotonously with the increase in the reaction temperature to reach about 18% at 653 K (Fig. 4). The phenomenon shows clearly that the thermodynamic limitation of the reaction (1) is removed by the addition of zeolite.



However, it should be noted that when the data in Fig. 4 are compared with those shown in Fig. 1, the yield of products is apparently lower below 573 K for the hybrid catalyst. The hydrocarbon yield itself is lower than that which has been obtained with a hybrid catalyst composed of Cu-Zn-Al mixed oxide and H-Z (15) (dotted line in Fig. 4). Since the activities of methanol formation are about the same for each catalyst, the low activity of the complex cata-

lyst containing Pd/SiO<sub>2</sub> is most likely attributed to the poisoning effect by some product, presumably aromatic hydrocarbons. Product pattern is rather constant between 523 and 623 K, where the selectivity of aromatic hydrocarbons lies between 40 and 50% (carbon base). However, the aromaticity of the product decreases with increasing temperature above 623 K which accompanies the sharp increases in methane and propane. The increased yield in methane at higher temperature is attributed to the high selectivity of methane in the hydrogenation of CO on the Pd/SiO<sub>2</sub> catalyst.

When the H<sub>2</sub>/CO ratio in the feed gas decreases from 2.0 to 0.5, product yield based on carbon monoxide fed decreases from 11 to 4% (Fig. 5). However, since the content of CO in the feed is twice-higher, the decrease in the productivity (STY) is only 30%. The change in the selectivity is characterized, on the other hand, by a marked increase in the aromatic hydrocarbons from about 30 to about 70%. It should also be noted that C<sub>8</sub> and C<sub>9</sub> aromatics, which are scarcely formed from synthesis gas with a H<sub>2</sub>/CO ratio of 2.0, make up 10% of the total aromatics. The low H<sub>2</sub>/CO ratio indicate the low hydrogenation activity of Pd/SiO<sub>2</sub>; therefore, the product pattern is thought to be affected not only by the rela-

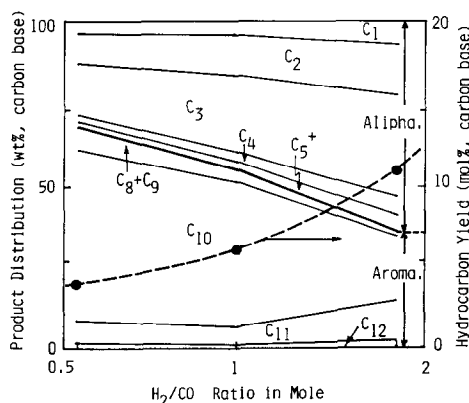


FIG. 5. Effect of H<sub>2</sub>/CO mole ratio on the synthesis gas reaction over a hybrid catalyst. Pd-SiO<sub>2</sub>/H-Z = 1/1 (weight ratio); P = 2.06 MPa; Temp. = 623 K; W/F = 9 g · h/mol.

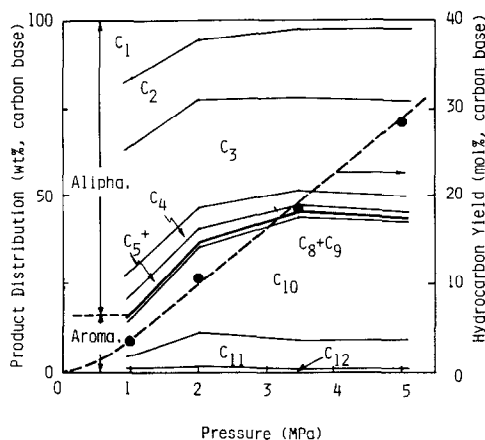


FIG. 6. Pressure effect on the synthesis gas reaction over a hybrid catalyst. Pd-SiO<sub>2</sub>/H-Z = 1/1 (weight ratio); H<sub>2</sub>/CO = 2/1; Temp. = 623 K; W/F = 9 g · h/mol.

tive rate of methanol synthesis and its conversion (catalyst composition) but also by the successive hydrogenation of the intermediate products.

The data shown in Fig. 6 make it clear that the yield of hydrocarbons increases almost proportionally to the reaction pressure accompanied by an increase in the selectivity of aromatic hydrocarbons up to 45% (carbon base) at 3.55 MPa. The increase in product aromaticity with increasing reaction pressure would be attributed to the high concentration of methanol in the catalyst bed (6).

As shown in Fig. 7, the yield of hydrocarbons is almost proportional to the time factor from 1.5% (W/F = 1.0 g-cat · h/mol) to 22.4% (W/F = 20 g-cat · h/mol) with the product pattern almost unchanged. It suggests that secondary reactions, such as hydrogenation of aromatic hydrocarbons or hydrocracking of aliphatic paraffins and methyl benzenes are of no significance and that the rate of synthesis gas conversion is zero-order with respect to carbon monoxide. The zero-order on the carbon monoxide pressure coincides with that of methanol formation on a supported palladium catalyst (18). It should be also noted that at a very early stage of the reaction the selectivity of C<sub>7</sub> to C<sub>9</sub> aromatics is fairly high

while that of pentamethyl benzene is low. This fact suggests that lowly methylated aromatics are first formed and are then successively methylated very quickly.

#### Discussions on the Factors Affecting the Yield and Pattern of Product

Characteristic features of the total hydrocarbon yield in synthesis gas reactions on the hybrid catalysts which are summarized as (i) the hydrocarbon yield increases monotonously with increased reaction temperature and pressure, and (ii) the yield is almost proportional to the time factor, indicate that the thermodynamic equilibrium between synthesis gas and methanol is removed and thus the hydrocarbon yield is controlled by the kinetics. However, the small differences in the activity between catalysts with different compositions makes it difficult to identify the rate-determining step of hydrocarbon formation.

Product patterns in the Pd/SiO<sub>2</sub> + H-Z catalyst system are characterized as

- (i) Little aliphatic olefins are formed.
- (ii) The major aromatic hydrocarbons are tetramethyl and pentamethyl benzenes.
- (iii) The higher selectivity of aromatic hydrocarbons is favored by reaction condi-

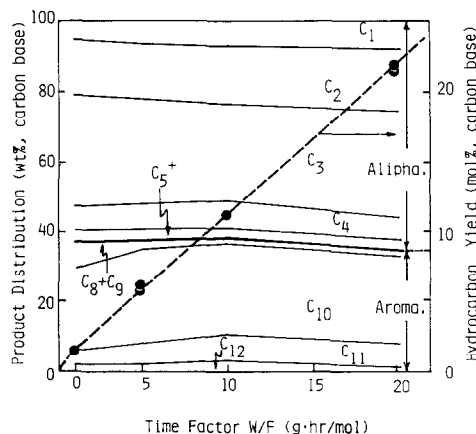


FIG. 7. Effect of time factor on the synthesis gas reaction over a hybrid catalyst. Pd-SiO<sub>2</sub>/H-Z = 1/1 (weight ratio); H<sub>2</sub>/CO = 2/1; P = 2.06 MPa; Temp. = 623 K.

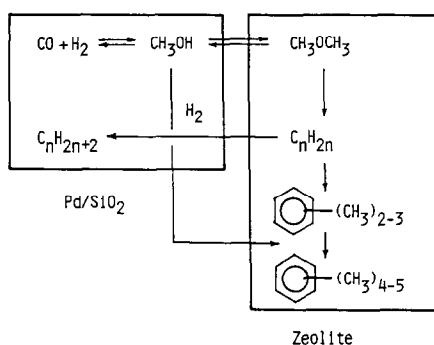


Fig. 8. Reaction scheme of CO hydrogenation on the hybrid catalyst composed of Pd-SiO<sub>2</sub> and zeolite.

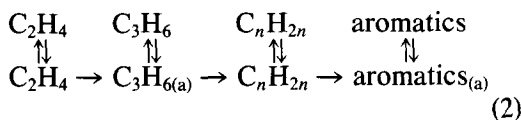
tions where the hydrogenation ability of the hybrid catalysts is low.

(iv) Reactions under high pressure give products which are high aromaticity.

(v) The change in the time factor has little effect on the product distribution except in the very early stage.

They suggest a reaction scheme shown in Fig. 8. The main part of the scheme is, of course, composed of methanol formation on the Pd/SiO<sub>2</sub> catalyst and methanol conversion on the H-ZSM-5 zeolite via dimethyl ether. The existence of both catalyst components so closely to each other brings about two new reactions as shown in Fig. 8. The first one is the catalytic hydrogenation of aliphatic olefins which are the intermediates from methanol to aromatic hydrocarbons as well as the hydrogen acceptor for aromatization (5), on the palladium catalyst. The second one is the successive methylation of aromatic hydrocarbons by methanol to polymethyl benzenes.

The path from lower olefins to aromatic hydrocarbon is (13)



Therefore, light olefins which are desorbed from zeolite surface are repeatedly adsorbed on zeolite to polymerize to higher olefins and finally to aromatic hydrocar-

bons. Otherwise, they pick up hydrogen atoms on the zeolite surface to form paraffins. However, in the case where the Pd/SiO<sub>2</sub> catalyst, which is a highly active catalyst for olefin hydrogenation, exists closely to zeolite, olefins in the gas phase have a chance to be adsorbed on either zeolite or palladium. When they are adsorbed on palladium they would be hydrogenated by hydrogen in the gas phase. Whereas carbon monoxide is well known to be a strong poison for olefin hydrogenation on palladium catalysts, the high temperature would enable the reaction even in the presence of high pressure of carbon monoxide.

The high selectivity of ethane in the synthesis gas conversion system compared to the methanol conversion system is also explained by the scheme. Ethylene, although it has low reactivity on H-ZSM-5 (9, 19), probably due to its low ability to form carbonium ion, would react slowly to form higher olefins on zeolite without being hydrogenated. This is due to its low ability to pick up hydrogen from zeolite. For the synthesis gas conversion system, on the other hand, ethylene in the gas phase would be mostly hydrogenated on the Pd/SiO<sub>2</sub> catalyst due to the high reactivity of hydrogenation.

The high selectivity of tetramethyl and pentamethyl benzenes for the synthesis gas conversion system, which are scarcely formed in the methanol conversion on H-ZSM-5 due to its shape selectivity (5), can also be interpreted by the secondary methylation of aromatic hydrocarbons. Since methanol is mostly converted to olefins at the initial stage of the reaction in the methanol conversion system (5, 6) only olefins exist in the reaction zone of aromatization. Thus, the reagent for the successive alkylation of the product aromatic hydrocarbon is olefins. However, the alkylation by olefins of benzenes should be very difficult due to the small pore of the zeolite (4). Thus the formation of either polymethylated benzenes or benzene derivatives with larger alkyl radicals is quite small. On the other

hand, methanol is formed everywhere in the catalyst bed for the synthesis gas conversion system. The methylating reagent (methanol or dimethyl ether) exists even in the lower part of the catalyst bed where lowly methylated products such as toluene and xylene exist in high concentrations. Methylation of benzene derivatives by methanol on zeolite is effectively catalyzed by H-ZSM-5 and other zeolites (20, 21). The formation of methyl benzenes with 5 or more methyl groups, which are hard to be formed on H-ZSM-5 due to shape selectivity, would be most likely attributed to the catalytic action of acid sites on the outer surface of the zeolite, whose amount has been estimated to occupy a few percentage of the total acid amount (9, 22).

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