# Hydrogenation of Carbon Monoxide on CO Reducing Catalyst and Solid Acid (III). The Effect of the Pore Size and Acid Properties of Zeolite on the Product Distribution

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Synthesis gas reactions over hybrid catalysts composed of $Pd/SiO_2$ and zeolites and methanol conversion on the same zeolites were studied. The selectivities to aromatic hydrocarbons were about 30% for the methanol conversions over ZSM-5, de-aluminated mordenite, and de-aluminated Y type zeolite (DAY), which possess strong acid sites. When ZSM-5 or mordenites were combined with $Pd/SiO_2$ and subjected to synthesis gas conversion, the selectivities to aromatic hydrocarbons were between 10% and 30%. However, the synthesis gas reaction over the hybrid catalyst composed of $Pd/SiO_2$ and DAY, gave few aromatic hydrocarbons, but aliphatic paraffins with 2 to 6 carbon atoms. Over large pore zeolites like DAY, the diffusion of olefins is so quick that most of the olefins come out of pores to be hydrogenated to paraffins on the $Pd/SiO_2$ catalyst. In contrast, because of the slow diffusion of olefins in the medium size pores of ZSM-5 or mordenite, olefins stay in the pores for long enough to form aromatic hydrocarbons on the strong acid sites before being hydrogenated.

It has been reported that synthesis gas is converted over a mixture of Zn–Cr oxides or Zr oxide and ZSM-5 at a temperature of 427 °C and a pressure of 83 atm to produce gaseous and liquid hydrocarbons rich in aromatics.[1]

Such synthesis gas reactions over hybrid catalysts composed of methanol synthesis catalysts and zeolites can mitigate the thermodynamic constraint of methanol formation because of the successive conversion, in situ, of the methanol to hydrocarbons over the zeolites. When a Cu–Zn–Al methanol synthesis catalyst was used in combination with H–ZSM-5 or H–Y at 10—20 atom and 250—380 °C, aliphatic hydrocarbons with 3 to 6 carbon atoms were obtained with a high selectivity, but few aromatic hydrocarbons were formed.[2] In the case of reactions over a hybrid catalyst composed of $Pd/SiO_2$ and ZSM-5, polymethylbenzenes were obtained with a high selectivity.[2-3] Similar studies of hydrocarbon synthesis from synthesis gas over several hydrid catalysts containing Cu–Zn–Pd and Zn–Cr catalysts have also been reported.[4-5]

This study attempted to clarify the charateristic feature of various zeolites as components of the hydrid catalysts containing $Pd/SiO_2$ from the standpoint of the direct synthesis of aromatic hydrocarbons from synthesis gas and to elucidate the effects of the zeolite catalyst on the product distributions.

## Experimental

*Catalyst Preparation and the Synthesis Reaction.*        A $Pd/SiO_2$ catalyst (Pd 4wt%) was prepared by impregnating a commercially available silica gel (Fuji Davison ID; specific surface area: 270 $m^2$; pore volume: 1.1cc/g; mean pore diameter: 140 Å) with palladium chloride from its acidic aqueous solution by a dry up method. Then the catalyst precursor was dried in an air oven at 120 °C for 20 h and

reduced in flowing hydrogen at 400 °C for 4 h.

Na–ZSM-5 type zeolite was synthesized according to the method described in the literature.[6] H–ZSM-5 was prepared from Na–ZSM-5 by ion-exchanging with hydrochloric acid (1 M=1 mol $dm^{-3}$) at 70 °C for a week, followed by drying at 120 °C for 20 h and calcining at 500 °C for 3 h. The crystallinity of ZSM-5 was measured by X-ray diffractometry, which showed that it was high enough to use in this study. The other zeolites were commercially available substances. H–M(A) (Zeolon 100H mordenite from Norton Co.), H–M(B) (Zeolon 900H mordenite from Norton Co.), RE–Y (Linde type SK-500) and Linde type Aw-500 were activated by calcining at 400 °C for 3 h. H–Y, H–L, and H–X were prepared from Linde type SK-40, Linde type SK-45, and Na–X respectively by treating them 5 times with an aqueous $NH_4Cl$ solution, followed by drying at 120 °C for 20 h and by calcining at 450 °C for 3 h. The DAY (de-aluminated Y type zeolite) was supplied by Shokubai Kasei, Inc. The DAM (de-aluminated mordenite) was prepared from Zeolon 100H (mordenite) by treating it with an aqueous hydrochloric acid solution (8 M) for 24 h. The physical and acidic characters of zeolites are listed in Table 1.

The hybrid catalyst was prepared and activated as follows: Portions of $Pd/SiO_2$ and zeolite of equal weights were mixed physically and then crushed to powder under an 80 mesh. Then they were pressed into a disk and finally crushed to granules with 20—40 mesh. About 2.0 g of the hybrid catalyst was placed in a tublar reactor (6 mm in inner diameter) and was activated in flowing hydrogen at 400 °C for 2 h. Then the synthesis gas reaction was conducted.

A pressurized flow type-reaction apparatus was used for the synthesis gas reaction. The apparatus was equipped with an electronic temperature controller, a furnace, a tublar reactor, a flow regulator-controller and a back-pressure regulator. All products were withdrawn from the reactor in the gaseous state and were and analyzed gas chromatographically.

For the methanol conversion experiment, zeolites were pressed into disks and crushed to granules with 20—40 mesh. H–M(B), RE–Y, and Aw-500 extrudates were crushed to granules with 20-40 mesh. About 1.0 g portion of

zeolite granules were placed in the tublar reactor and activated in the same way as that of the hybrid catalyst. The methanol reactions were conducted, using the same apparatus as that used for the synthesis gas reaction, by passing through a gaseous mixture of methanol vapor and hydrogen or nitrogen.

*Determination of the Acidic Features of Zeolites.* About a 200 mg protion of zeolite was put in a glass cell and then evacuated at 500 °C for 2 h. Then the first isotherm of ammonia adsorption was measured at room temperature. After evacuating for 1 h at room temperature, the second isotherm was determined. The difference between the two isotherms, which is defined as the ammount of ammonia chemisorbed, was defined as the "acidity" of the zeolite.

The temperature programmed desorption (TPD) of ammonia on zeolites was measured by heating the sample at the rate of 7.6 °C/min. The desorbed ammonia was measured with a mass spectrometer. (Anelva TE-150). A site which liberated ammonia above 300 °C was defined as a strong acid site.

## Results

*Acidic Features of the Zeolites.* Figures 1,2,3, and 4 show the TPD spectra of ammonia for various zeolites, where $\theta$ is the coverage and $T$ is the desorption temperature. It should be noted that the vertical axes $(-\mathrm{d}\theta/\mathrm{d}T)$ of the Figures indicate the fraction of desorbed ammonia at each temperature, therefore, the integration of each spectrum for all the temperature range is unity. The acidities of the various zeolites, as measured by means of the ammonia chemisorption, are shown in Table 1. As has previously been reported,[2] the spectrum of H-ZSM-5 has two peaks; one is at around 100 °C, and the other is at around 350 °C. The spectrum of H-M(A), similarly to H-ZSM-5, has a low temperature peak at around 100 °C and a high temperature peak at around 350 °C. In the case of DAM, the acidity is apparently smaller than that of the parent mordenite (Table 1), and both the peaks of TPD were shifted to temperatures

higher by about 100 °C. These facts indicate that the acid strength of mordenite was promoted by the extraction of aluminium. Although the acidity of H-Y is large, its TPD spectrum shows only one peak, at around 100 °C, indicating that the amount of strong acid sites is quite small. RE-Y, which contains a rare earth metal ion, exhibits a spectrum
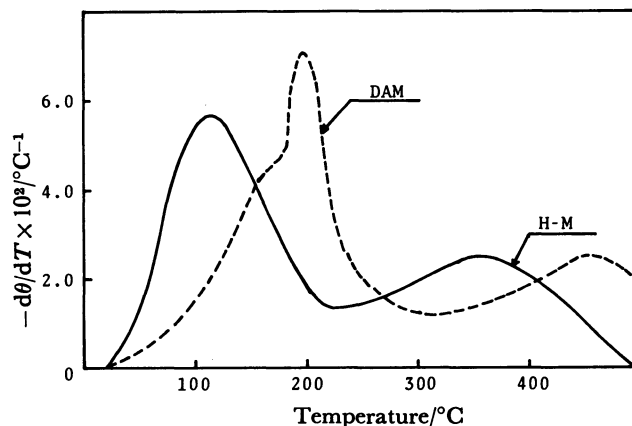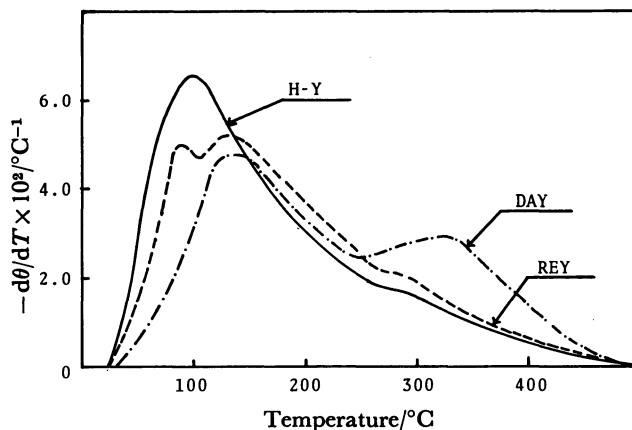


Fig. 2. TPD Profiles of NH₃ from Mordenites.



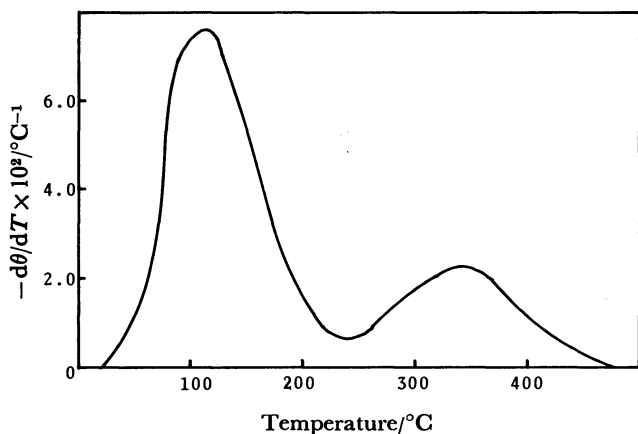Fig. 3. TPD Profiles of NH₃ from Y Type Zeolites.

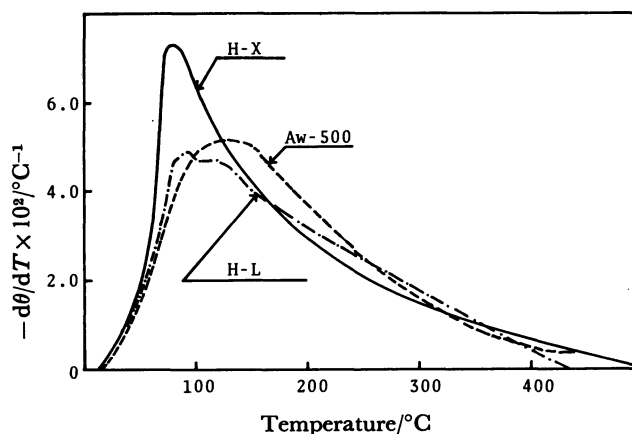

Fig. 1. TPD Profiles of NH₃ from H-ZSM-5.



Fig. 4. TPD Profiles of NH₃ from Various Zeolites.

TABLE 1.  PHYSICAL AND ACIDIC CHARACTERISTICS OF ZEOLITES USED

| Zeolite | Acidity (mmol/g) | Content of aluminium (mmol/g) | $SiO_2/Al_2O_3$ molar ratio | Fraction of strong acid sites (%) | Pore size (Å)[a] |
|---------|------------------|-------------------------------|------------------------------|-----------------------------------|-------------------|
| H-ZSM-5 | 1.74 | 1.2 | 50.2 | 25.7 | 6 |
| H-M(A) | 3.74 | 2.0 | 14.6 | 32.6 | 6.9 |
| H-M(B) | — | 2.8 | 10 | — | 6.9 |
| DAM | 1.52 | 0.6 | 53.0 | 37.5 | 6.9 |
| H-Y | 4.63 | 5.1 | 4.8 | 10.2 | 13 |
| DAY | 4.22 | 3.6 | 7.6 | 27.0 | 13 |
| REY | — | 4.5 | 4.9 | 11.2 | 13 |
| H-X | 9.33 | 7.9 | 2.5 | 11.4 | 13 |
| H-L | 4.55 | 3.9 | 5.4 | 16.3 | 7.1 |
| Aw-500 | — | 2.8 | 10 | 9.3 | 4.0 |

a) Data from Ref. 7.

TABLE 2.  RESULTS OF METHANOL CONVERSION OVER ZEOLITE CATALYSTS

| Catalyst | H-ZSM-5 | H-M(A) | DAM | DAY | H-M(B) | H-Y |
|----------|---------|--------|-----|-----|--------|-----|
| Reaction conditions | | | | | | |
| Temperature (°C) | 350 | 350 | 350 | 332 | 350 | 350 |
| Pressure (atm) | 1 | 15 | 15 | 21 | 15 | 15 |
| W/F (g-cat·h/mol) | 4.6 | 4.4 | 4.9 | 4.6 | 4.8 | 4.9 |
| MeOH conc. (mol%) | 10.0 | 1.1 | 1.4 | 10 | 1.1 | 1.1 |
| Balance Gas | $N_2$ | $H_2$ | $H_2$ | $H_2$ | $H_2$ | $H_2$ |
| Hydrocarbon yield/% | 100 | 100 | 100 | 65 | 100 | 100 |
| Hydrocarbon distributions (C-wt%) | | | | | | |
| Methane | 0.5 | 10.9 | 2.2 | 1.5 | 2.3 | 7.7 |
| Ethane | tr. | 18.8 | 6.7 | 1.3 | 16.0 | 14.6 |
| Ethene | 3.4 | tr. | tr. | 7.1 | 2.1 | 0.7 |
| Propane | 9.5 | 30.4 | 22.1 | 2.7 | 14.7 | 12.4 |
| Propene | 3.7 | tr. | tr. | 8.8 | 0.2 | 0.9 |
| Butane | 4.4 | 6.4 | 10.8 | 10.2 | 4.2 | 4.0 |
| Isobutane | 17.9 | 6.9 | 21.1 | | 43.2 | 31.2 |
| Butenes | 3.6 | tr. | tr. | 3.8 | tr. | tr. |
| $C_5$+Aliphatics | 26.7 | 3.9 | 7.1 | 34.1 | 16.7 | 28.3 |
| Benzene | tr. | 0.3 | 0.6 | — | — | — |
| Toluene | 8.1 | 2.5 | 2.0 | 0.6 | — | — |
| Xylenes | 12.6 | 5.7 | 2.9 | 0.9 | — | — |
| Trimethylbenzenes | 7.6 | 7.2 | 1.2 | 1.8 | — | — |
| Tetramethylbenzenes | 1.3 | 4.9 | 0.2 | 2.3 | — | 0.2 |
| Pentamethylbenzene | 0.4 | 0.9 | 10.5 | 4.7 | — | — |
| Hexamethylbenzene | 0.1 | 1.1 | 12.3 | 20.1 | — | — |
| $C_{13}$+Aromatics | — | — | 0.4 | — | — | — |
| Selectivity to aromatics | 30.4 | 22.6 | 30.1 | 30.5 | 0 | 0.2 |
| H/C ratios in products | 1.9 | 2.5 | 2.3 | 2.0 | 2.6 | 2.8 |

similar to that of H-Y. DAY, whose acidity is smaller than that of H-Y, as is demonstrated in Table 1 shows a TPD spectrum with two peaks; one is at around 130 °C, and the other is at around 330 °C. It indicates that strong acid sites were generated by extracting aluminium. The TPD spectra of Aw-500, H-X, and H-L exhibit single peaks at around 100 °C.

*Reaction of Methanol.*    Products from methanol

conversion over the zeolites, which were measured at 3—4 h after the start of the reaction, are shown in Table 2 and they may be summarized as follows:

(1)  Every zeolites tested except H-M(B) and H-Y gave aromatic hydrocarbons with selectivities of around 30% (carbon base).

(2)  The $C_2$ and $C_3$ hydrocarbons were composed of both olefins and paraffins.

(3) De-aluminated zeolites (DAY and DAM) gave aliphatic hydrocarbons with a higher molecular weight and aromatic hydrocarbon with a higher selectivity, compared with their parent zeolites.

(4) All zeolites gave $C_4$ paraffins rich in iso-butane.

(5) While the major aromatic hydrocarbons obtained with H-ZSM-5 were di- or trimethylbenzenes, the main aromatics formed over DAM and DAY were $C_{11}$ aromatics and $C_{12}$ aromatics (mostly pentamethylbenzene and hexamethylbenzene respectively).

(6) Every zeolite tested except H-ZSM-5 lost its activity within a few hours.

TABLE 3. CONVERSION OF CO OVER Pd/SiO₂ CATALYSTS

| Temperature | Yield[a] | | | |
|---|---|---|---|---|
| °C | MeOH | H.C. | CO₂ | DME |
| 250 | 2.3 | 0.02 | — | — |
| 280 | 4.8 | 0.1 | — | — |
| 300 | 4.2 | 0.2 | — | — |
| 330 | 1.8 | 0.6 | 0.6 | 0.17 |
| 350 | 0.8 | 1.1 | 1.0 | 0.23 |
| 370 | 0.7 | 1.2 | 1.4 | 0.33 |

a) Yield in mol% of carbon monoxide fed, 21 atm, $W/F = 5$ g-cat·h/mol, $H_2/CO = 2$,

(7) The excess hydrogen in the product hydrocarbon ($H/C > 2$) indicates that a large amount of carbonaceous material (coke) was deposited on all the zeolites except ZSM-5 during the reaction.

(8) The facts that over DAY, which possesses a fairly large amount of strong acid sites, aromatic hydrocarbons were formed whereas H-Y, which possesses few strong acid sites, gave no aromatic hydrocarbons, are consistent with the suggestion that aromatic hydrocarbons are formed on the strong acid sites.[8]

*Methanol Synthesis with Pd/SiO₂.* The methanol synthesis activity of the Pd/SiO₂ used in this study is shown in Table 3. The maximum methanol yield was obtained at around 300 °C. Above 300 °C, the yield of methanol decreased markedly with increase in the temperature, presumably because of the thermodynamical limitation. The yields of oxygenates (methanol plus dimethyl ether) and hydrocarbons (90% methane, and the rest, ethane) were about 1.0% and 1.1% respectively at 350 °C, where the synthesis gas reactions were mostly studied.

*Synthesis Gas Conversion over the Hybrid Catalysts.* The results of synthesis gas conversion with the hybrid catalysts composed of the Pd/SiO₂ and various zeolites are shown in Table 4. The data were examined with particular attention paid to (1) the catalytic activity, (2) the carbon number distribution

TABLE 4. HYDROGENATION OF CARBON MONOXIDE OVER VARIOUS HYBRID CATALYSTS[a]

| Zeolite[b] | ZSM-5 | H-M(A) | H-M(B) | DAM[c] | H-Y[c] | DAY[c] | REY | Aw-500 | H-L | H-X |
|---|---|---|---|---|---|---|---|---|---|---|
| Yields of | | | | | | | | | | |
| Hydrocarbons | 9.6 | 8.0 | 9.8 | 9.7 | 6.5 | 14.6 | 8.4 | 7.3 | 6.4 | 3.6 |
| Carbon dioxide | 5.4 | 3.3 | 4.2 | 7.2 | 2.7 | 5.9 | 7.7 | 3.4 | 6.1 | 3.3 |
| Oxygenates | — | — | — | — | — | — | — | — | 1.6 | 3.3 |
| Hydrocarbon distributions (C-wt%) | | | | | | | | | | |
| Methane | 12.4 | 12.6 | 25.1 | 6.0 | 12.6 | 16.3 | 10.9 | 13.8 | 33.8 | 96.9 |
| Ethane | 13.3 | 39.7 | 29.7 | 22.7 | 22.3 | 18.2 | 23.4 | 30.3 | 31.8 | 2.4 |
| Ethene | tr. | 0.2 | 0.1 | 0.2 | tr. | tr. | tr. | tr. | tr. | — |
| Propane | 33.2 | 24.6 | 18.5 | 28.1 | 29.2 | 32.8 | 31.1 | 36.1 | 17.7 | 1.0 |
| Propene | 0.1 | 0.2 | 0.1 | 0.2 | tr. | tr. | tr. | tr. | tr. | — |
| C-4 | 6.2 | 5.3 | 7.4 | 16.6 | 21.7 | 22.2 | 26.1 | 12.8 | 11.2 | — |
| C-5 | 2.3 | 2.2 | 2.3 | 4.9 | 9.3 | 1.5 | 2.2 | 1.9 | 2.9 | — |
| C-6⁺ Aliph. | 1.9 | 4.2 | 2.0 | 2.3 | 4.9 | 1.5 | 2.2 | 1.9 | 2.9 | — |
| Benzene | — | 0.2 | — | — | — | — | — | — | — | — |
| Toluene | — | 0.1 | — | — | — | — | — | — | — | — |
| Xylenes | 0.1 | 0.7 | — | — | — | — | — | — | — | — |
| Tri. M.B.[d] | 1.4 | 0.7 | 0.1 | 0.1 | — | 0.1 | — | — | — | — |
| Tetra. M.B.[d] | 21.9 | 1.2 | 0.5 | 1.8 | — | 0.6 | — | — | — | — |
| P.M.B.[d] | 6.9 | 5.1 | 9.0 | 15.2 | — | 0.2 | — | — | — | — |
| H.M.B.[d] | 0.3 | 2.6 | 4.1 | 1.8 | — | — | — | — | — | — |
| C-13⁺ Aroma. | — | 0.1 | 1.1 | — | — | — | — | — | — | — |
| Selectivity to aromatics | 30.6 | 10.7 | 14.8 | 18.9 | — | 0.9 | — | — | — | — |
| iso-C₄/n-C₄ | 0.22 | 0.89 | 0.68 | 0.27 | 1.05 | 0.66 | 0.85 | tr. | 0.96 | — |

a) Hydrogenated at 370 °C, 21 atm, $W/F = 10$ g-cat·h/mol, $H_2/CO = 2$, b) Zeolite of which hybrid catalyst composed, c) Hydrogenated at 350 °C, d) Tri. M.B. = Trimethylbenzenes; Tetra. M.B. = Tetramethylbenzenes; P.M.B. = Pentamethylbenzene; H.M.B. = Hexamethylbenzene.

of product hydrocarbon, (3) the selectivity to aromatic hydrocarbons, and (4) the content of olefin and branched products in aliphatic hydrocarbons.

The yields of hydrocarbons on the hybrid catalysts were in the range of 3—15%, much higher than those of methanol on the $Pd/SiO_2$ catalyst alone. For each hybrid catalyst, the main product was hydrocarbon. Small amounts of oxygenates, mainly methanol and dimethyl ether, were also formed when H-L and H-X were combined with the $Pd/SiO_2$ catalyst.

The selectivities of aromatic hydrocarbons lie between 0—30%, depending on the zeolites used. These results will be discussed later. There are two peaks in the carbon number distribution of the product hydrocarbons; one is at $C_2$ or $C_3$ (aliphatic hydrocarbons), while the other is at $C_{10}$ or $C_{11}$ (aromatic hydrocarbons). For the catalysts which contain Y type zeolite as one component, the products were mostly aliphatic hydrocarbons with 1 to 4 carbon atoms. It is worthwhile to note that the conversion of synthesis gas on the hybrid catalysts composed of DAY and $Pd/SiO_2$ gave few aromatic hydrocarbons, whereas the conversion of methanol on DAY gave hexamethylbenzene with fairly high selectivities.

The data of the olefin contents of $C_2$ and $C_3$ hydrocarbons shown in Table 4 indicate clearly that the formation of olefins is quite small on the hybrid catalysts. However, methanol is converted into olefins at a fairly high selectivity on the zeolites, as is exemplified in Table 2. The low selectivity of olefins in the case of synthesis gas conversion is attributed to the hydrogenation of olefins on the $Pd/SiO_2$ catalyst, as has already been indicated by the present authors.[3]

The $iso$-$C_4/n$-$C_4$ ratio, representing the degree of chain branching of aliphatic hydrocarbons, lies between 0 and 1.1, and it depends strongly on the zeolite employed.

## Discussion

*Formation of Lower Paraffins.*    A comparison of the data in Tables 2 and 4 shows that the selectivities to lower paraffins in the synthesis gas reaction over hybrid catalysts are higher than those of methanol conversion over zeolite catalysts. As has already been mentioned,[3] the products of the synthesis gas reaction over the hybrid catalysts are seriously influenced by the hydrogenation of olefins on the $Pd/SiO_2$ catalyst along the path shown in Fig. 5. Lower olefins, which are the key intermediates from methanol to aromatic hydrocarbons, are hydrogenated over the $Pd/SiO_2$ catalyst to inert paraffins, which are stable under the present reaction conditions. Thus, the selectivities to lower paraffins are higher for the synthesis gas reaction than for the methanol conversion on zeolites alone.

*Formation of Branched Chain Paraffins.*    It is apparent from the data shown in Tables 2 and 4 that the

$iso$-$C_4/n$-$C_4$ ratios in the products of synthesis gas reaction are smaller than those of methanol conversion. The low value of the $iso$-$C_4/n$-$C_4$ ratio in the products of synthesis gas reactions are also attributable to the hydrogenation of olefins on the $Pd/SiO_2$ catalyst. Most paraffins are formed through the hydrogenation of olefins on the $Pd/SiO_2$ catalyst, as has been described above. Since the skeletal isomerization of olefins can be assumed to be very fast over a zeolite catalyst, the composition of olefins should be at equilibrium. Therefore, the formations of linear and branched paraffins are on the same level if the hydrogenation reactivities of both olefins are on the same level, because the $iso$-$C_4H_8/n$-$C_4H_8$ ratio is not high at the equilibrium state.

In contrast, paraffins are thought to be formed, during the methanol conversion on zeolite, by hydrogen transfer,[8] that is, carbonium ions on the zeolite pick up hydride ions from other hydrocarbons during the formation of aromatics or coke. Because of the higher stability of the tertiary carbonium ion, its concentration would be higher than that of the secondary carbonium ion; thus, the formation of branched hydrocarbon would be predominant. The models of both reaction paths are shown in Fig. 6.

The ratios of $n$-$C_4$ to $iso$-$C_4$ in the products from synthesis gas $vs.$ the pore diameter of zeolites or the super-cage size of faujasites (H-X, H-Y, and DAY) shown in Fig. 7 indicate that the selectivity to $iso$-$C_4$ is higher for the zeolite with larger pores. This fact is interpreted in terms of the shape selectivity of zeolites. That is, the formation of bulky $iso$-$C_4$ (5.6 Å)[9] is hard in small pore zeolite such as Aw-500, whose pore diameter is about 4 Å. It should also be noted that the ratios of $iso$-$C_4$ to $n$-$C_4$ in the $C_4$ paraffins obtained over the catalysts containing DAM or DAY are lower than those for the catalysts containing their parent zeolites, which possess a larger acidity.

*Formation of Aromatic Hydrocarbons.*    Figure 8 shows how the selectivity of aromatic hydrocarbons correlates to the fraction of strong acid sites and the pore diameter of zeolite. It clearly shows that aromatic hydrocarbons are formed only with the hydrid catalysts containing the zeolites whose fractions of strong acid
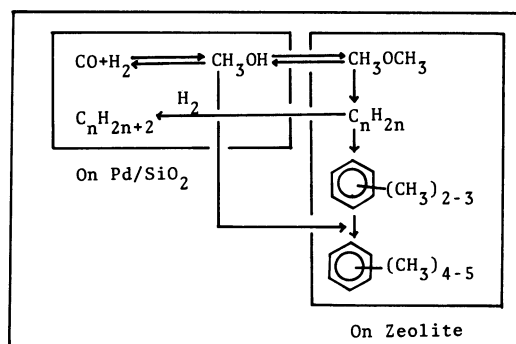


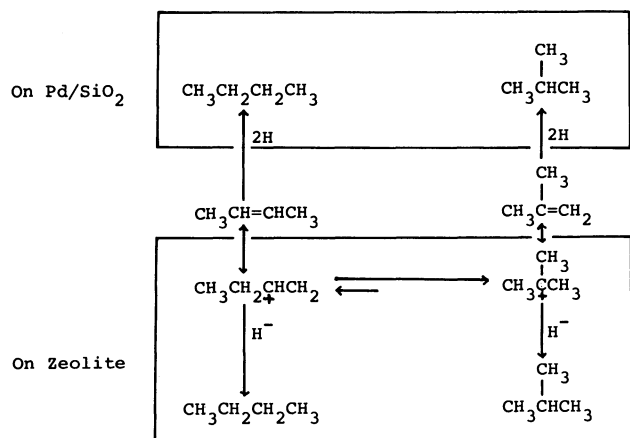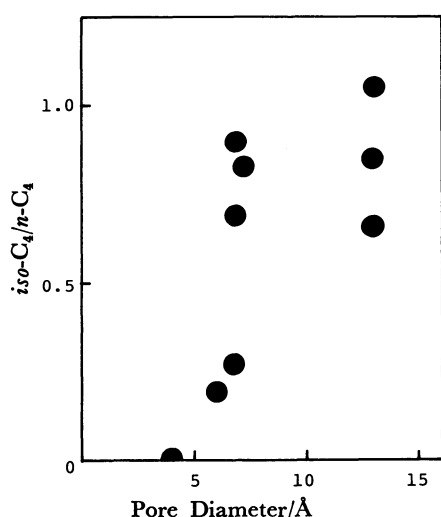Fig. 5.   Reaction Scheme on Hybrid Catalysts.

Fig. 6. Chain Branching.



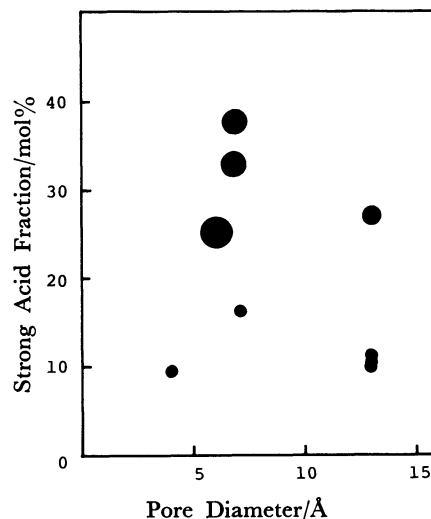Fig. 7. A Ratio of $n$-$C_4$ to $iso$-$C_4$ vs. Pore Diameter.



Fig. 8. Strong Acid Fraction and Selectivity to Aromatic Hydrocarbons vs. Pore Diameter.

● : Selectivity to Aromatics was more than 20%.
● : Selectivity to Aromatics was between 10% and 30%.
● : Selectivity to Aromatics was between 0% and 10%.
● : Selectivity to Aromatics was 0%.

site are higher than 20% and whose pore diameter lie between 6 and 7 Å. It should be noted that there is no relationship between the amount of strong acid sites and the selectivity to aromatic hydrocarbons. For example, the amounts of strong acid site of H-ZSM-5 and H-Y are 0.45 and 0.47 mmol/g respectively. On the hybrid catalyst containing H-ZSM-5, synthesis gas gave aromatic hydrocarbons with a high selectivity, while no aromatic hydrocarbons were formed on the H-Y containing catalyst. The hydrid catalyst containing H-M(A), whose amount of strong acid site is 1.22 mmol/g, gave aromatic hydrocarbons with a selectivity of around 10%, while the hybrid catalyst containing DAM, whose amount of strong acid sites is 0.57 mmol/g, gave aromatic hydrocarbons with a selectivity of around 20%.

Again, the formation of aromatic hydrocarbons is strongly related to the fraction of strong acid sites (Figure 8). This fact is interpreted as follows: The methanol formed on the Pd/SiO₂ is converted to olefins on both weak and strong acid sites.[10] Some of the olefins formed are converted to aromatic hydrocarbons

on the acid site, while others are hydrogenated to the inert paraffins by means of hydrogen transfer on both weak and strong acid sites or by catalytic hydrogenation on the Pd/SiO₂. Consequently, the product distribution is controlled by the relative rate of aromatization and hydrogenation. Therefore, the fraction of strong acid sites (or the ratio of the amount of strong acid sites to that of weak acid site) is an important factor in determining the selectivity to aromatic hydrocarbons.

It is also shown the selectivity to aromatic hydrocarbons is strongly related to the pore diameter of the zeolite contained in the hybrid catalysts. It is strange that DAY gives few aromatic hydrocarbons when it is combined with Pd/SiO₂ and subjected to synthesis gas reaction although it has enough strong acid sites to produce aromatic hydrocarbons from methanol, as is shown in Table 2. This is also interpreted in terms of the diffusion of olefins from the zeolite pores to the Pd/SiO₂ and the successive hydrogenation to inert paraffins on it.

As is shown in Fig. 9, olefins formed from methanol on the zeolite can not be converted into aromatic hydrocarbons on a small pore zeolite like Aw-500, as is demonstrated in Table 4, where it is hard for even $iso$-$C_4$ to be formed. Thus, olefins are hydrogenated to inert paraffins on the palladium catalyst without being converted to aromatic hydrocarbons. In the case of the hybrid catalysts containing large pore zeolites, like DAY, which have the ability to form aromatic hydrocarbons, the diffusion of olefins is so quick that most of them come out of the pores before being converted into

aromatics, and they reach the palladium catalyst, where they are easily hydrogenated to paraffins. By contrast, in the case of zeolite with medium size pores (6—7 Å), like ZSM-5 or mordenites, olefins stay in the pores for long enough to be converted into aromatic hydrocarbons over the strong acid sites before being hydrogenated to paraffins, because of the slow diffusion of olefins in the pores. Although H-L has a medium size pore (7.1 Å), the fraction of strong acid sites is not enough to form aromatic hydrocarbons. Therefore, olefins formed in the pore will slowly diffuse to the Pd/SiO₂ catalyst without being converted into aromatic hydrocarbons and then hydrogenated to inert paraffins.

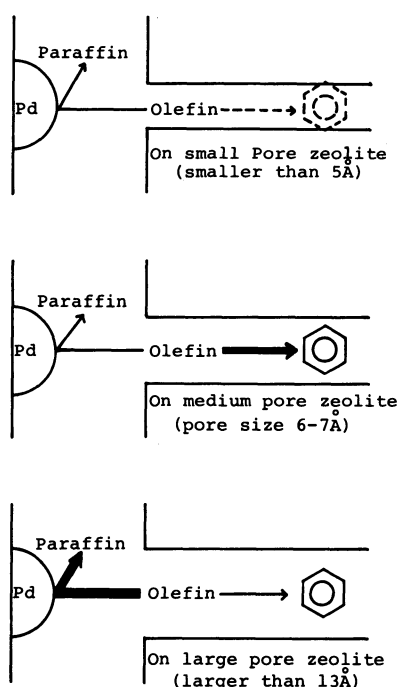The product distribution obtained by methanol



Fig. 9.    Effect of Pore Diameter on Formation of Aromatic Hydrocarbons.

conversion on ZSM-5 and DAM and by synthesis gas conversion on the hybrid catalysts containing ZSM-5 and DAM are compared in Fig. 10. It is apparent that, over both catalysts, the aliphatic hydrocarbons formed from synthesis gas are lower in molecular weight than those obtained by methanol conversion and that aromatic hydrocarbons are more highly methylated in the synthesis gas conversion. These characteristics can be attributed to the hydrogenation of lower olefins and to the successive methylation of product methylbenzenes, which have previously been indicated by the present authors.[3]

## Conclusion

The conversion of synthesis gas over hybrid catalysts composed of Pd/SiO₂ and zeolites gave the following conclusions:

(1)   The main hydrocarbons formed are $C_1$—$C_3$ paraffins and polymethylbenzenes,

(2)   The ratio of linear to branched paraffins in the product hydrocarbon is higher for zeolites with larger pores and larger acidities,

(3)   The extraction of aluminium in zeolites is effective for increasing strong acid sites, which is essential for the formation of aromatic hydrocarbons,

(4)   Aromatic hydrocarbons are formed over the zeolites whose strong acid fraction is higher than 20% of the total acid sites and whose pore size lies between 6 and 7 Å.

## References

1)   C. D. Chang, W. H. Lang, and J. Silvestri, *J. Catal.*, **56**, 268 (1979).

2)   K. Fujimoto, Y. Kudo, and H. Tominaga, *Nippon Kagaku Kaishi*, **1982**, 206.

3)   K. Fujimoto, Y. Kudo, and H. Tominaga, *J. Catal.*, **87**, 136 (1984).

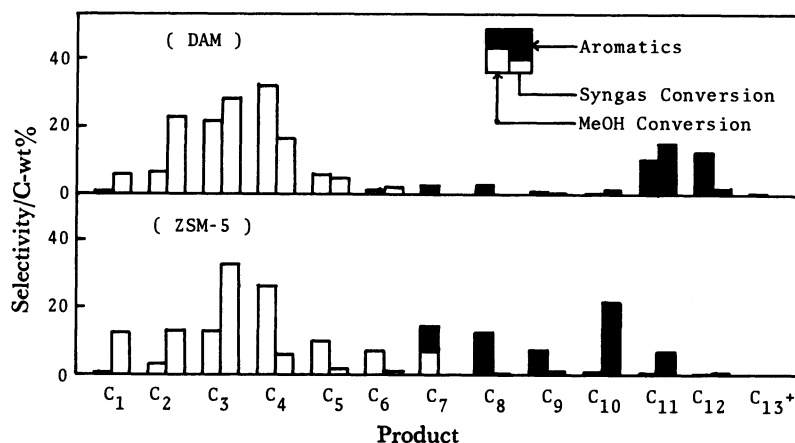4)   T. Yashima, A. Yoshimura, Y. Wakushima, and S.



Fig. 10.    Comparison of Syngas Conversion on Hybrid Catalyst and Methanol Conversion on Zeolite Catalyst alone.

Namba, Pan Pacific Synfuel Conference, Tokyo, November 1982, Preprints, No. B3.

5) T. Inui and Y. Takegami, Pan Pacific Synfuel Conference, Tokyo, November 1982, Preprints, No. B5.

6) A. Yoshimura, S. Namba, and T. Yashima, *Shokubai*, **23**, 232 (1981).

7) D. W. Breck, "Zeolite Molecular Sieves," John Wiley&Sons, New York, (1974), Chap. 2.

8) P. Dejaifve, J. C. Vedrine, V. Bolis, and E. G. Derouane, *J. Catal.*, **63**, 331 (1980).

9) N. Hara, "Zeolite To Sono-riyou," ed by H. Takahashi, Gihoudou Shuppan, Tokyo (1967), p. 144.

10) T. Imai, K. Iida, H. Fujita, T. Haruki, and N. Yokoyama, *Shokubai*, **23** (1), 99 (1981).