

## [Regular Paper]

# Synthesis of Liquefied Petroleum Gas via Methanol and/or Dimethyl Ether from Natural Gas (Part 1) Catalysts and Reaction Behaviors Associated with Methanol and/or Dimethyl Ether Conversion

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Synthesis of liquefied petroleum gas (LPG) from methanol and/or dimethyl ether (DME) was investigated over various zeolite catalysts. H-ZSM-5 with the MFI structure was confirmed to be the optimum catalyst for selective LPG synthesis. Effects of the silica–alumina ratio in H-ZSM-5 on the methanol or DME conversion were also investigated. The conversion of methanol or DME was maximum at a silica–alumina ratio of 50 or 90, respectively. Selectivities towards LPG hydrocarbons improved with increasing silica–alumina ratio for both feeds. The correlation between catalytic performance of the selected H-ZSM-5 catalyst and kinetic factors in methanol conversion was also examined. The operating conditions for the formation of C<sub>3</sub>–C<sub>4</sub> hydrocarbons were identified by optimizing gas hourly space velocity and reaction temperature as well as feed partial pressure, *e.g.*, 20,000–30,000 h<sup>-1</sup>, > 400°C, and > 45 kPa, with a system pressure of about 120 kPa. LPG fractional hydrocarbons could be formed selectively from methanol, DME, or a mixed feed. Addition of steam to the nitrogen used as diluent gas led to a decrease in DME conversion.

## Keywords

Natural gas, Liquefied petroleum gas, Methanol conversion, Dimethyl ether conversion, Zeolite catalyst, Synthetic fuel

## 1. Introduction

Effective utilization of natural gas is one of the long-standing problems in the synfuel and petrochemical fields. Over the past three decades, various routes, both direct and indirect, have been considered for transforming natural gas into high-quality fuels or petrochemicals<sup>1)</sup>. In the present decade, methanol conversion to hydrocarbons has been the object of extensive research<sup>2)</sup>, and two main processes, methanol-to-gasoline (MTG) and methanol-to-olefins (MTO), have been demonstrated commercially in respective pilot plants<sup>2),3)</sup>, but the changing market situation worldwide has not provided the conditions required for commercialization, which depends on the demand and price. Apparently, commercial applications of methanol to hydrocarbon conversion still requires some further breakthrough. In fact, research continues on methanol-to-hydrocarbon processes<sup>4)</sup>. Previous R&D efforts have constructed the fundamental technologies covering both catalytic materials and hydrocarbon processing, which will be beneficial for new technological development through

other transformation routes. Most previous research concerning zeolite catalysts for methanol conversion has focused on production of automobile gasoline or chemicals under special conditions. The formation of liquefied petroleum gas (LPG) synthesis from natural gas has attracted little attention.

A new concept with respect to LPG synthesis for utilizing natural gas has been developed very recently<sup>4)</sup>. The proposed LPG process has two modes: direct use of synthesis gas, which consists of *in-situ* two steps through intermediate methanol; and sequential conversion *via* methanol and/or dimethyl ether (DME), which is mainly based on methanol-to-hydrocarbon technologies. Both modes are intended to produce LPG from natural gas. LPG widely used as domestic fuel and is likely to show further growth as a clean vehicle fuel in the future. On the other hand, the potentially greater demand for LPG, previously supplied by oil refineries so far, will inevitably accelerate the consumption of limited petroleum resources. Therefore, local processing of natural gas instead of petroleum could meet the prospective market requirement.

The proposed indirect process protocol combines main operating units for natural gas reforming, raw methanol or DME production, LPG hydrocarbon syn-

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thesis (C<sub>3</sub>-C<sub>4</sub> olefins and paraffins) and saturation hydrogenation, which have all been experimentally demonstrated in our previous work<sup>5</sup>).

The present study investigated the catalytic performance and structural properties of typical zeolite species, according to pore size as well as channel dimensionality that reflects the connectivity of pore systems, for the indirect heterogeneous catalytic LPG process. The main kinetic factors affecting catalytic performance were examined in detail using the optimized H-ZSM-5 catalyst with a higher silica-alumina ratio. Conversion of methanol and DME co-feed was investigated to clarify the use of intermediate feeds, and the addition of steam to nitrogen as diluent gas investigated in DME to LPG hydrocarbons. The range of possible zeolite-based catalysts and the suitable conditions for selective conversion of methanol and/or DME to LPG hydrocarbons were identified, and the basic characteristics allowing improvement in the selectivity and stability of catalysts, as well as the possibility of forming propene, were investigated.

## 2. Experimental

### 2.1. Zeolite Synthesis and Pretreatment

The various crystalline MFI-metallosilicates, MWW and MTF-aluminosilicates, and two silicoaluminophosphate (SAPO) molecular sieves were hydrothermally synthesized as described previously<sup>6-8</sup>. The solid products were submitted to standard procedures: drying at 120°C overnight, calcining at 550°C for 4 h, ion exchange of original cations with 1 mol/l NH<sub>4</sub>Cl solution, and conversion to the H-form by calcination at 550°C for 2 h. The zeolites, H-ZSM-5 with silica-alumina ratios of about 50 or 90, and protonated Beta were prepared in our laboratory, and Zeolite USY was obtained as a commercial product. The crystallinity and phase purity of these synthesized and pretreated materials were characterized by X-ray powder diffraction.

### 2.2. Catalyst Preparation

All catalysts consisted of prefabricated zeolite (65 wt%) and Al<sub>2</sub>O<sub>3</sub> (35 wt%), with pseudoboehmite (Catalysts Chemicals Ind. Co., Ltd.) as a binder. The extrusion molding predecessors of catalysts were dried at 120°C for 24 h and calcined at 550°C for 8 h, and formed into pellets with average diameter of 0.85 mm.

### 2.3. Reaction Tests

The reaction tests for methanol or DME conversion were carried out in a slightly pressurized fixed-bed reactor at 330 to 450°C. Normal experiments lasted for 6 h. The catalyst was placed in the stainless steel tube reactor of 300 mm length, 8 mm inside diameter, with a 20 mm section in the middle equipped with a cell of thermocouples for controlling the temperature distribution. The reaction gas mixtures consisted of methanol (or DME) and N<sub>2</sub> controlled to a gas hourly

space velocity (GHSV) of 18,000-48,000 h<sup>-1</sup>, feed partial pressure of 30-70 kPa and total pressure of 120 (or 170) kPa at the required temperatures. All products were gathered and analyzed by three gas chromatograph units on line with hydrogen-flame ionization detector (FID) or thermal conductivity detector (TCD). All data used were uniform at the point of 3 h on-stream for different runs, and were calculated on a carbon basis.

## 3. Results and Discussion

### 3.1. Selection of Zeolite Species for LPG Synthesis Catalysts

For the methanol-to-hydrocarbon reaction, the inner pores of zeolite catalysts are generally assumed to be a sterically controlled reaction space compared with macroporous or homogeneous catalysts. Therefore, the great diversity of structure and composition among zeolites results in intrinsic properties such as acid-catalyzed activity and shape-selectivity. Hydrocarbon product distributions in methanol and/or DME conversion are expected to be confined to the desired carbon-number ranges based on the pore sizes, possible supercages, and dimensions. These considerations of structure-reactivity features in zeolite chemistry have encouraged the use of various zeolites, typically classed into small-, medium- and large-pore types<sup>9</sup>, as methanol or DME conversion catalysts. Typical results are compiled in **Table 1**, together with recent results concerning SAPO-34, SAPO-5, H-Beta and H-USY catalysts<sup>5</sup>, which systematically illustrate the effects of zeolite structures on catalytic performance.

The small-pore H-MCM-35 and SAPO-34 catalysts selectively form C<sub>1</sub>-C<sub>3</sub> hydrocarbons with coke deposits, which are heavier for these two catalysts than for other catalysts. H-MCM-35 (MTF) with 8-member rings and unidimensional channels preferentially forms methane and ethene compared to SAPO-34 with identical openings but three-dimensional channels. These small-pore zeolites favor very narrow product distributions due to the more severe steric restrictions for methanol conversion inside these zeolites, resulting in methane formation. Therefore, most of the resulting products are outside the LPG fraction.

Large-pore zeolite catalysts, such as SAPO-5 and H-Beta, selectively convert methanol to the LPG fraction but the C<sub>3</sub> hydrocarbon contents are too low to provide a high-quality LPG fuel, and heavy byproducts, C<sub>5</sub><sup>+</sup> non-aromatics and aromatics, are formed rather than light C<sub>1</sub>-C<sub>2</sub> fractions, implying that the shape selectivities in methanol conversion are quite poor compared with the small- and medium-pore zeolites. H-USY catalyst reveals intermediate activity in the methanol-to-hydrocarbon conversion and offers a wider hydrocarbon distribution compared with SAPO-5 and H-Beta

Table 1 Lower Hydrocarbon Synthesis from Methanol over Various Zeolite Catalysts<sup>a)</sup>

| Catalyst (zeolite species)   |                    | H-MCM-35    | SAPO-34       | H-ZSM-11    | H-ZSM-5     | H-MCM-22 <sup>b)</sup>     | SAPO-5        | H-Beta      | H-USY       |
|--|--------------------|-------------|---------------|-------------|-------------|----------------------------|---------------|-------------|-------------|
| Pore size  | [nm] <sup>c)</sup> | 0.36 × 0.39 | 0.38 × 0.38   | 0.53 × 0.54 | 0.53 × 0.56 | 0.41 × 0.51<br>0.40 × 0.55 | 0.73 × 0.73   | 0.76 × 0.64 | 0.74 × 0.74 |
| Ring member of main channels <sup>d)</sup>   |                    | 8           | 8-8-8         | 10-10-10    | 10-10-10    | 10-10, 12                  | 12            | 12-12       | 12-12-12    |
| SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> /(P <sub>2</sub> O <sub>5</sub> ) (mole ratio in gel) |                    | 120/1.0     | 0.6/1.0/(0.8) | 52.0/1.0    | 50.0/1.0    | 45.0/1.0                   | 0.6/1.0/(0.8) | 25.6/1.0    | 12.2/1.0    |
| Reaction temperature   | [°C]               | 330         | 400           | 400         | 400         | 400                        | 400           | 367         | 400         |
| Methanol conversion  | [%]                | 19.5        | 17.9          | 90.5        | 98.4        | 57.2                       | 22.3          | 77.6        | 44.3        |
| Yield of LPG hydrocarbons  | [%]                | 0.1         | 4.3           | 55.2        | 68.5        | 31.4                       | 11.6          | 34.5        | 19.8        |
| Hydrocarbon distribution   | [%]                |             |               |             |             |                            |               |             |             |
| Methane  |                    | 18.5        | 13.9          | 1.2         | 1.2         | 2.5                        | 7.6           | 0.9         | 9.6         |
| Ethane   |                    | 0.0         | 0.0           | 0.4         | 0.2         | 0.0                        | 0.5           | 0.2         | 0.0         |
| Ethene   |                    | 58.5        | 17.2          | 7.4         | 12.0        | 4.5                        | 8.4           | 7.3         | 16.5        |
| Propane  |                    | 0.2         | 16.0          | 5.5         | 2.7         | 1.2                        | 4.0           | 2.2         | 0.5         |
| Propene  |                    | 0.4         | 8.1           | 24.4        | 37.6        | 30.7                       | 14.4          | 10.9        | 23.2        |
| Butanes  |                    | 0.0         | 0.0           | 13.6        | 8.6         | 6.6                        | 15.4          | 25.8        | 5.1         |
| Butenes  |                    | 0.0         | 0.0           | 17.5        | 19.6        | 16.3                       | 18.0          | 5.6         | 16.0        |
| C <sub>5</sub> <sup>+</sup> nonaromatics   |                    | 0.0         | 0.0           | 11.5        | 5.5         | 18.7                       | 3.7           | 19.1        | 2.3         |
| Aromatics  |                    | 22.4        | 44.8 (coke)   | 18.5        | 12.6        | 19.4                       | 28.0          | 28.0        | 26.8        |
| C <sub>1</sub> -C <sub>2</sub> hydrocarbons  |                    | 77.0        | 31.2          | 9.0         | 13.4        | 7.0                        | 16.5          | 8.4         | 26.1        |
| C <sub>3</sub> -C <sub>4</sub> hydrocarbons  |                    | 0.6         | 24.1          | 61.0        | 68.5        | 54.9                       | 51.8          | 44.5        | 44.8        |
| C <sub>5</sub> <sup>+</sup> and aromatics  |                    | 22.4        | 44.8          | 30.0        | 18.1        | 38.1                       | 31.7          | 47.1        | 29.1        |
| C <sub>3</sub> /(C <sub>3</sub> + C <sub>4</sub> )   | [%]                | 100         | 100           | 49.0        | 58.9        | 58.2                       | 35.5          | 29.4        | 52.9        |

a) GHSV = 30,000 h<sup>-1</sup>, carrier gas: N<sub>2</sub>, methanol partial pressure: 45 kPa, total pressure: 120 kPa; and all reaction data are calculated on the carbon basis. Results for SAPO-34, SAPO-5, H-Beta and H-USY catalysts are cited from our previous work<sup>5)</sup>.

b) The values (0.41 × 0.51 and 0.40 × 0.55) are the openings of 10-ring channels viewed normal to [001] within layers and between layers, respectively, and there is no direct connection between the two pore systems, but the MWW cages viewed along [001] with dimensions of 1.82 × 7.1 × 7.4 nm<sup>3</sup> contain 12-ring windows located in the opening 'cup' to the surface or each of two half-cages<sup>10)</sup>.

c) Data for the pore structure is taken from the literature<sup>9)</sup>.

d) H-ZSM-11 and H-ZSM-5 zeolites have three-dimensional 10-member ring channels without accessible micropores along the [001] direction; H-Beta has three-dimensional 12-member ring channels without accessible micropores along the [010] direction. Information of main channel dimensions is also offered, for example, 10-10-10 for H-ZSM-5 refers to the presence of three 10-member ring channels along three independent directions which are intersecting but not necessarily perpendicular.

zeolites. The wider hydrocarbon distribution may be ascribed to the open faujasite structure, in which each zeolite unit consists of a supercage connected with four (12-ring) channels along the tetrahedral orientations. These large-pore zeolites, with unidimensional or even tridimensional channels, are apparently not suitable for LPG synthesis from methanol.

Three representative medium-pore zeolites, H-ZSM-11, H-ZSM-5 and H-MCM-22, generally exhibit good catalytic performance in methanol conversion and LPG fractional selectivities compared with both small- and large-pore zeolites as mentioned above. The medium-porous crystalline aluminosilicates, H-ZSM-5 with MFI structure, show extraordinary performance in catalytic activity, selectivity and C<sub>3</sub> content in the total C<sub>3</sub>-C<sub>4</sub> hydrocarbons. Zeolite H-MCM-22 has been confirmed to supply effective active sites for formation of substituted aromatics larger than C<sub>8</sub> and the C<sub>5</sub><sup>+</sup> aliphatics<sup>11)</sup>. H-MCM-22 catalyst forms an extremely low ratio of ethene with a slightly higher ratio of propene, but the precise details are unclear. H-ZSM-5 catalyst is superior to H-ZSM-11 and H-MCM-22 for shape-selective formation of C<sub>3</sub>-C<sub>4</sub> hydrocarbon. In addition, specific features of various zeolite catalysts, *e.g.*, surface acidity, active site distribution, etc., also affect the catalytic performance in methanol conversion.

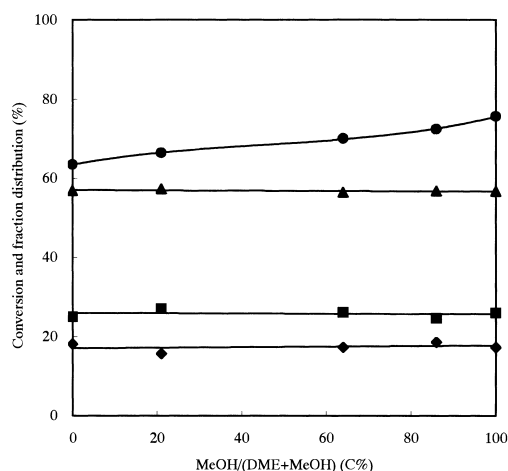
Overall, H-ZSM-5 (MFI) catalyst is the optimum catalyst known for selectively converting methanol into LPG hydrocarbons.

### 3. 2. Conversion of Methanol and DME Co-feeds

Conversion of co-feeds of methanol and DME was examined using H-ZSM-5 (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 50) catalyst. Lower reaction temperature was applied to distinguish the reactivities of co-feeds with different compositions. As shown in **Fig. 1**, methanol, DME and the mixture could be selectively converted into LPG hydrocarbons. Selectivities for the C<sub>1</sub>-C<sub>2</sub> fraction, LPG hydrocarbons and C<sub>5</sub><sup>+</sup> plus aromatics remained almost unaffected by the feed composition. Total conversion of co-feeds to hydrocarbons increased with increasing methanol content, suggesting different affinities of methanol and DME molecules for the H-ZSM-5 catalyst. **Figure 2** reveals that the C<sub>3</sub> and paraffin contents in the formed LPG hydrocarbons did not depend on the feed composition. These results demonstrate that methanol and DME are both suitable as intermediate feeds for the proposed LPG process.

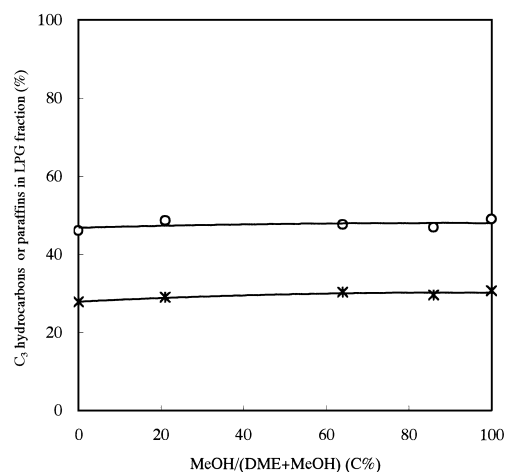
### 3. 3. Effect of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>

A previous investigation<sup>5)</sup> has indicated that the catalytic performance of H-ZSM-5 catalysts obviously depends on the silica-alumina ratio and that a silica-alumina ratio of about 50 is optimum for catalyzing methanol conversion at a relatively low temperature (330°C). The effect of silica-alumina ratio on both methanol and DME conversion to LPG hydrocarbons at a preferable reaction temperature (400°C) is shown in



Co-feed partial pressure 34-45 kPa, total pressure 120 kPa, GHSV 30,000 h<sup>-1</sup> and temperature 330°C.

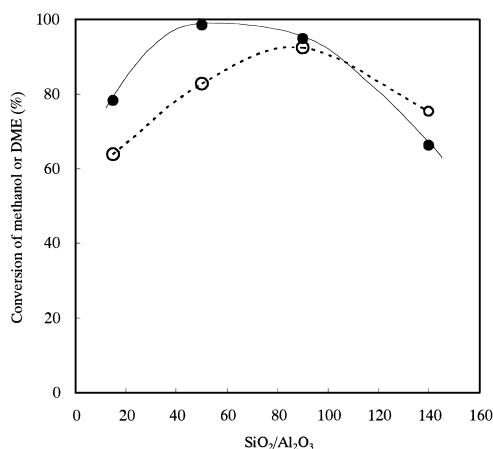
Fig. 1 Methanol and DME Co-feed Conversion to LPG Hydrocarbons over H-ZSM-5 (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 50) Catalyst under Reaction Conditions



○ C<sub>3</sub>/(C<sub>3</sub>+C<sub>4</sub>), \* Paraffins in LPG fraction.

Fig. 2 C<sub>3</sub>-hydrocarbon Percentage and Saturation of LPG Hydrocarbons vs. Co-feed Compositions at 330°C

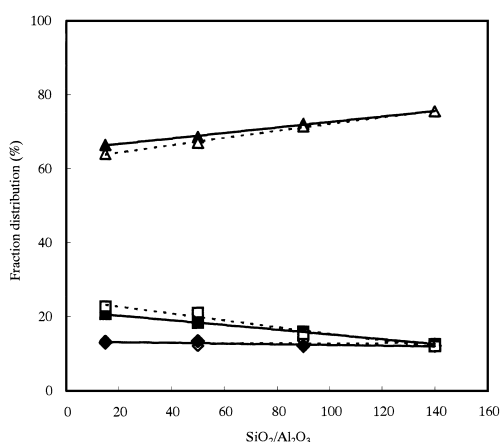
**Fig. 3.** The conversion maxima emerge at silica-alumina ratios of about 50 and 90 for methanol and DME feeds, respectively, and methanol reacts more actively than DME over catalysts with silica-alumina ratios of less than 90. The results of conversion as a function of time on-stream (results not shown) revealed that the deactivation of various catalysts gradually increased with decreased silica-alumina ratio, although the initial conversions were close to complete conversion. The quasi-stable state was considered as the uniform point at 3 h on-stream. Therefore, the conversions of both feeds were relatively low with low silica-alumina ratio,



● Methanol, ○ DME.

Methanol partial pressure 45 kPa, DME partial pressure 34 kPa, total pressure 120 kPa, GHSV 30,000 h<sup>-1</sup> and temperature 400°C.

Fig. 3 Conversion of Methanol or DME as a Function of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> in H-ZSM-5 under Reaction Conditions

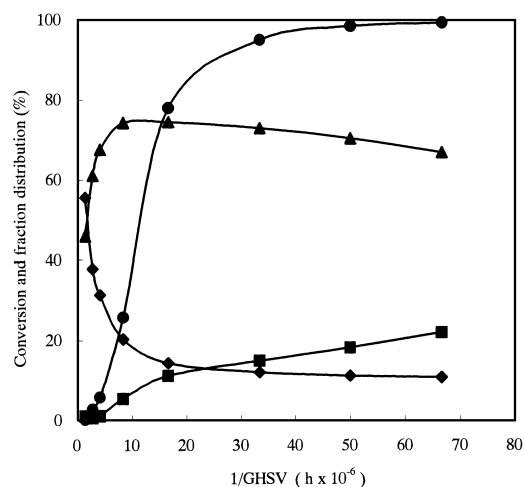


▲ C<sub>3</sub>+C<sub>4</sub>(MeOH), △ C<sub>3</sub>+C<sub>4</sub>(DME), ◆ C<sub>1</sub>+C<sub>2</sub>(MeOH), ◇ C<sub>1</sub>+C<sub>2</sub>(DME), ■ C<sub>5</sub><sup>+</sup> and aromatics(MeOH), □ C<sub>5</sub><sup>+</sup> and aromatics(DME).

Fig. 4 Effect of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> Ratio of H-ZSM-5 on Fraction Distributions in Methanol or DME Conversion

whereas methanol conversion was relatively high compared to DME. On the other hand, the DME conversion increased gradually and then exceeded methanol conversion with increasing silica-alumina ratio. The DME reaction behavior is different to that of methanol with greater silica-to-alumina ratio, and can be ascribed to variations in hydrophobic property of H-ZSM-5 catalysts<sup>12)</sup> and the diversity in molecular polarity. The reactivity of each feed generally falls with increasing silica-alumina ratio, possibly due to reduction in the number of available active sites.

Figure 4 shows the various fraction distributions related to the silica-alumina ratio. The selectivity for



● Conversion, ▲ C<sub>3</sub>+C<sub>4</sub>, ◆ C<sub>1</sub>+C<sub>2</sub>, ■ C<sub>5</sub><sup>+</sup> and aromatics.  
H-ZSM-5, temperature 400°C, methanol partial pressure 45 kPa and total pressure 120 kPa.

Fig. 5 Methanol Conversion and Fraction Distribution as Functions of Gaseous Space Time

LPG hydrocarbons is improved with increasing silica-to-alumina ratio. The improvements in C<sub>3</sub>-C<sub>4</sub> intermediate selectivities were always associated with decreases in conversion under given reaction conditions. In addition, selectivities for both light and heavy fractions were also lower with increasing silica-alumina ratio. The monotone increase in selectivity for LPG hydrocarbons may be attributed to the decrease in acid density on the catalysts, which is a function of the silica-alumina ratio and affects the conversion depth of these oxygenates. To increase both the yield of LPG hydrocarbons and the resistance to deactivation of catalysts, H-ZSM-5 with a silica-alumina ratio of about 90 was selected, in contrast with the previous work<sup>5)</sup>, for the following investigations. A more detailed discussion on other catalysts will be reported later.

### 3. 4. Kinetic Factors Affecting LPG Synthesis

#### 3. 4. 1. Gaseous Space Time

The complex consecutive reactions involved in the methanol-to-hydrocarbon conversion has already been the subject of kinetic investigations to conceptualize the reaction coordinate and network<sup>1),2)</sup>. Reaction contact time is always one of the conclusive factors to control the selectivity for the desired reaction in addition to the catalytic system. Figure 5 clearly shows the effect of increasing gaseous space time on the reaction of methanol to LPG hydrocarbons over the H-ZSM-5 catalyst. The conversion of methanol to LPG hydrocarbons gradually increases as a function of gaseous space time. Notice that a very rapid increase of methanol conversion is observed only with respect to

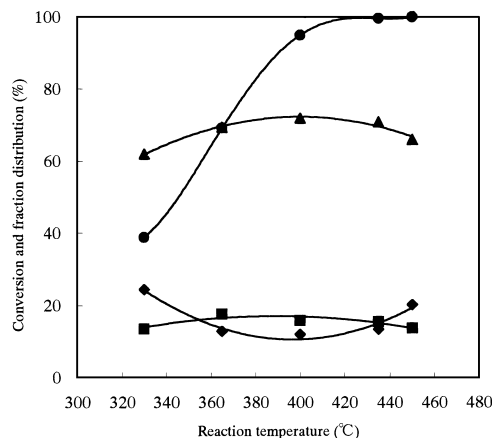


low gaseous space time. Two reasons are possible related to the sharp change of the S-shape conversion curve. First, an induction period for DME formation may be required since the methanol-to-hydrocarbon reaction must involve the formation of intermediate DME. This proposal can interpret the extraordinarily slow increase in methanol conversion within a very short contact time, but fails to explain the conversion curve leap, and a similar situation is also observed using DME only. In addition to the so-called induction effect, we consider that the other reason may be related to the required concentration of ethene intermediate or carbyne pool, which may promote the conversion of oxygenates.

Figure 5 also depicts the changes in the fraction distributions with increasing gaseous space time. The  $C_1$ - $C_2$  fraction, which consists of more than 95% ethene, decreases rapidly and associated with a sharp increase in the  $C_3$ - $C_4$  fraction with high propene content. These results may indicate the intermediate character of ethene formed in the LPG synthesis from methanol. Subsequently, the reaction selectivity for the  $C_1$ - $C_2$  fraction tends to stabilize with prolonged gaseous space time. This feature of the  $C_1$ - $C_2$  distribution implies that ethene selectivity may lie on the secondary olefin-equilibrium transformation when the gaseous contact time is longer. In the major product distribution, total  $C_3$ - $C_4$  fraction increases rapidly and then declines very slowly with an increase in gaseous space time. A further increase in gaseous space time results in a continuing increase in  $C_5^+$  non-aromatics and aromatics, although methanol approaches complete conversion. By demonstrating the methanol reaction behavior as a function of gaseous contact time, we conclude that both ethene and  $C_3$ - $C_4$  olefins exhibit intermediate nature, but that only the conversion of ethene to  $C_3$ - $C_4$  olefins results in the formation of LPG. This is a key issue to minimize reactions of  $C_3$ - $C_4$  olefins further towards higher olefins.

### 3. 4. 2. Reaction Temperature

The effect of increasing temperature on methanol conversion and fractional distribution of hydrocarbon products is revealed in Fig. 6. At constant gaseous space time ( $1/\text{GHSV}$ ) and feed partial pressure, methanol-to-hydrocarbon conversion over the H-ZSM-5 catalyst was accelerated by increasing reaction temperature, and complete conversion of methanol occurred at temperatures higher than  $435^\circ\text{C}$ . The  $C_3$ - $C_4$  fractional formation was also favored at high temperatures with respect to the formation of  $C_1$ - $C_2$  hydrocarbons or total aromatics and  $C_5^+$  non-aromatics. This is consistent with the earlier observations<sup>13</sup>. At low temperatures, ethene is the main byproduct but methane content is extraordinarily low. A moderate increase in reaction temperature caused thermodynamic shift of the product distribution towards the fractions of lower



● Conversion, ▲  $C_3+C_4$ , ◆  $C_1+C_2$ , ■  $C_5^+$  and aromatics. H-ZSM-5, GHSV 30,000  $\text{h}^{-1}$ , methanol partial pressure 45 kPa and total pressure 120 kPa.

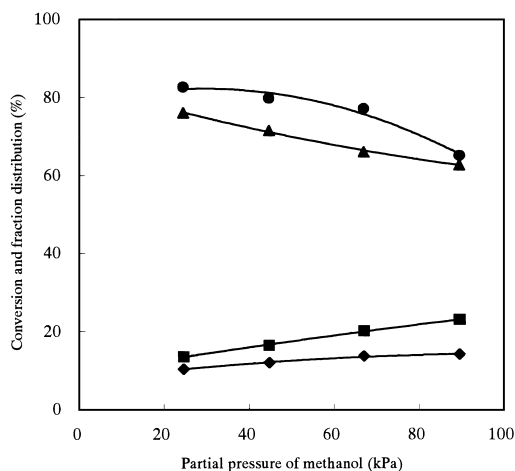
Fig. 6 Changes in Methanol Conversion and Fraction Distribution with Reaction Temperature

olefins, so butanes and especially propene became more important. In fact, the methanol-to-hydrocarbon reaction gradually departed from the well-known MTO reaction region. At higher temperatures, methanol conversion easily approached 100%. The  $C_1$ - $C_2$  fraction increased gradually and the fraction of total heavy byproducts decreased, although large  $C_8$ - $C_{10}$  aliphatics, naphthene and even  $C_8$  polyalkylated aromatics appeared. The variation in both light and heavy fractions is attributed to the secondary cracking of olefinic oligomers and heavy  $C_5^+$  non-aromatics at high temperatures in the presence of the acidic catalyst. Methane content also began to increase to a certain extent. Therefore, the optimum LPG synthesis from methanol catalyzed by the H-ZSM-5 catalyst proceeds in the range from  $400$  to  $435^\circ\text{C}$ .

### 3. 4. 3. Partial Pressure of Methanol

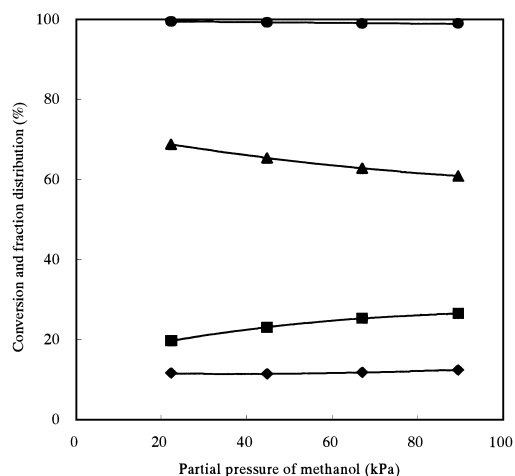
Figure 7 shows the effect of changing the methanol partial pressure on the methanol-to-hydrocarbon conversion under a gas hourly space velocity of  $60,000 \text{ h}^{-1}$ . The conversion of methanol decreased with increasing methanol partial pressure using such a high GHSV. The continuous reduction in the methanol conversion can be interpreted as increases in either methanol processing amount or generated water amount for a given amount of catalyst. The formation of the LPG fraction decreased gradually with methanol partial pressure. As expected, the formations of byproducts, either the heavy fraction or the light  $C_1$ - $C_2$  fraction, actually became unsuitable for production of LPG hydrocarbons.

Conversion with a low GHSV of  $18,000 \text{ h}^{-1}$  is shown in Fig. 8 with the same conditions applied in Fig. 7. The formations of various fractions exhibit similar behaviors with increasing partial pressure of methanol.



● Conversion, ▲ C<sub>3</sub>+C<sub>4</sub>, ◆ C<sub>1</sub>+C<sub>2</sub>, ■ C<sub>5</sub><sup>+</sup> and aromatics.  
H-ZSM-5, temperature 400°C, GHSV 60,000 h<sup>-1</sup> and total pressure 120 kPa.

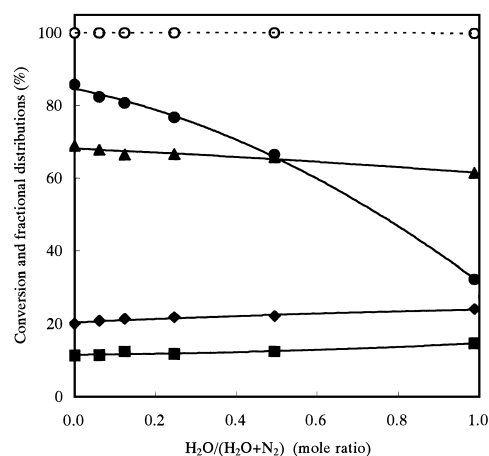
Fig. 7 Changes in Conversion and Fraction Distribution with Methanol Partial Pressure



H-ZSM-5, temperature 400°C, GHSV 18,000 h<sup>-1</sup> and total pressure 120 kPa.

Fig. 8 Changes in Methanol Conversion and Fraction Distribution with Methanol Partial Pressure

Nevertheless, the selectivity for the LPG fraction decreased and selectivity for the heavy fractions increased when methanol was converted completely into hydrocarbons under the low GHSV. Furthermore, diversity in C<sub>1</sub>-C<sub>2</sub> fractional selectivity was observed for the two cases. These observations may imply different pathways for formation of ethene. At very high GHSV (or low conversion), ethene may be formed mainly from methanol; at low GHSV (or nearly complete conversion), selectivity for ethene may be affected by the re-equilibration of all olefins.



○ Equilibrium conversion, ● Conversion, ▲ C<sub>3</sub>+C<sub>4</sub>, ◆ C<sub>1</sub>+C<sub>2</sub>, ■ C<sub>5</sub><sup>+</sup> and aromatics.  
H-ZSM-5, DME partial pressure 34 kPa, total pressure 170 kPa, GHSV 36,000 h<sup>-1</sup> and temperature 400°C.

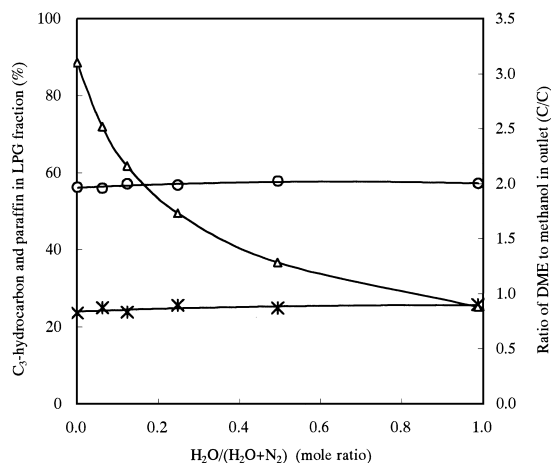
Fig. 9 Effect of Added Water Content in Diluent Gas on DME Conversion to LPG Hydrocarbons under Reaction Conditions

Operation under low partial pressure produces high-quality LPG hydrocarbons, but will result lower hydrocarbon current yield and the consumption for product recovery from the diluent gas in the downstream process.

### 3.5. Steam Content in Diluent Gas

Steam used as a carrier gas has advantages for cost, product separation and heat discharge. **Figure 9** shows the results of varying the content of added water in the diluent gas. Conversion of DME to hydrocarbons was considerably reduced with an increase in added water content and was far away from the thermodynamic equilibrium value under the same reaction conditions. We suggest that some negative effects on the used catalyst were caused by added water in the catalytic conversion of DME to hydrocarbons. The selectivity for C<sub>3</sub>-C<sub>4</sub> hydrocarbons declined slowly, whereas selectivities for the C<sub>1</sub>-C<sub>2</sub> hydrocarbons and the heavier hydrocarbon products increased monotonously. An analogous conclusion was reported using a jet loop reactor to convert methanol with water<sup>14)</sup>, as the influence of water generated from the methanol-to-hydrocarbon reaction could be disregarded. The benefits of added water announced by others could not be shown<sup>15)</sup>.

**Figure 10** depicts the C<sub>3</sub> content in the LPG fraction, saturation of formed LPG hydrocarbons and exit mole ratio of DME to methanol. The C<sub>3</sub> content in LPG hydrocarbons was almost independent of the added water, but the paraffin contents increased slowly. Only the variation in the ratio of DME to methanol was noticeable, which is strictly regulated by the thermody-



○ C<sub>3</sub>/(C<sub>3</sub>+C<sub>4</sub>), \* Paraffin in LPG fraction, △ DME/MeOH (mole ratio).

Fig. 10 C<sub>3</sub>-hydrocarbon and Paraffin Percentages in LPG Fraction and the Exit Ratio of DME to Methanol as Functions of Added Steam Content in Diluent Gas

namic equilibrium, indicating that MEOH-DME-H<sub>2</sub>O coexists along the reaction bed after co-feeding DME and steam. Therefore, competitive adsorption between water and the two oxygenates always occurs on the accessible active sites of the H-ZSM-5 catalyst and is responsible for the degeneration of catalytic activity.

#### 4. Conclusions

Various microporous zeolites were evaluated as catalysts for converting methanol and/or DME intermediates into LPG hydrocarbons. H-ZSM-5 (MFI) was confirmed as the most suitable for selective formation of LPG hydrocarbons. Changes in the silica-alumina ratio in H-ZSM-5 showed that conversion of methanol or DME is maximum at the silica-alumina ratio of about 50 or 90, respectively, and that selectivities for

LPG hydrocarbons always improved with increasing silica-alumina ratio for both feeds.

The optimum reaction conditions were obtained by uniting optimization of gaseous space time, reaction temperature and feed partial pressure. Over the H-ZSM-5 catalyst, methanol and/or DME can be selectively converted into LPG hydrocarbons under optimal conditions. Addition of steam to the nitrogen diluent gas lead to a decrease in DME conversion without obvious modification in hydrocarbon distribution.

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#### References

- 1) Dybekjær, I., Hansen, J. B., *Stud. Surf. Sci. Catal.*, **107**, 99 (1997).
- 2) Stocker, M., *Micropor. Mesopor. Mater.*, **29**, 3 (1999).
- 3) Keil, F. J., *Micropor. Mesopor. Mater.*, **29**, 49 (1999).
- 4a) Fujimoto, K., 8th Japan-China Symposium on Coal and C<sub>1</sub> Chemistry, 2003.
- 4b) Fujimoto, K., Saima, H., Tominaga, H., *J. Catal.*, **94**, 16 (1985).
- 5) Jin, Y., Asaoka, S., Li, X., Asami, K., Fujimoto, K., *Fuel Process. Tech.*, **85**, (8-10), 1151 (2004).
- 6) Gabelica, Z., Valange, S., *Micropor. Mesopor. Mater.*, **30**, 57 (1999).
- 7) Mochida, I., Eguchi, S., Hironaka, M., Nagao, S.-I., Sakanishi, K., Whitehurst, D., *Zeolites*, **18**, 142 (1997).
- 8) Prakash, A. M., Unnikrishnan, S., *J. Chem. Soc., Faraday Trans.*, **90**, 2291 (1994).
- 9) Venuto, P. B., *Micropor. Mater.*, **2**, 297 (1994).
- 10) Gopalakrishnan, G. J., Lobo, R. F., *Micropor. Mesopor. Mater.*, **40**, 9 (2000).
- 11) Ravishankar, R., Bhattacharya, D., Jacob, N. E., Sivasanker, S., *Micropor. Mater.*, **4**, 83 (1995).
- 12) Segawa, K., Sakaguchi, M., Nakata, N., Asaoka, S., *J. Chem. Soc. J.P., Chem. Ind. Chem.*, **3**, 528 (JP), (1989).
- 13) Chu, C. T. W., Chang, C. D., *J. Catal.*, **86**, 297 (1984).
- 14) Moller, K. P., Bohringer, W., Schnitzler, A. E., Steen, E. V., Connor, C. T. O., *Micropor. Mesopor. Mater.*, **29**, 127 (1999).
- 15) Chang, C. D., *Catal. Rev.-Sci. Eng.*, **26**, (3 & 4), 323 (1984).



## 要 旨

天然ガスからメタノールおよび／あるいはジメチルエーテル経由での液化石油ガス製造  
(第1報) メタノールおよび／あるいはジメチルエーテル転化における触媒と反応挙動

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ゼオライト触媒を用いてメタノールおよび／ないしジメチルエーテル (DME) を原料とした液化石油ガス (LPG) 合成を試みた。ゼオライトの中で MFI 構造を有する H-ZSM-5 が、選択的 LPG 合成に最も利用可能性の高いゼオライトであることが明らかとなった。また、H-ZSM-5 の  $\text{SiO}_2/\text{Al}_2\text{O}_3$  比のメタノールないし DME 転化に対する影響を検討した結果、この比の値がメタノールでは約 50 のとき、DME では約 90 のときに最高の転化率を示すことが分かった。しかしながら、LPG 成分への選択性は、どちらの原料のときも  $\text{SiO}_2/\text{Al}_2\text{O}_3$  比が増すと向上した。さらに本研究では、選定した H-ZSM-5 触媒を用いて、

触媒性能と動力学的因子の関係をメタノール転化の場合について検討した。ガス空時速度と反応温度および原料分圧を変えて検討した結果、 $\text{C}_3\text{-C}_4$  炭化水素生成に対する最適の運転条件は、 $20,000\sim 30,000\text{ h}^{-1}$ 、 $400^\circ\text{C}$ 、システム圧約 120 kPa のとき約 45 kPa であることが明らかとなった。メタノール、DME あるいはこれらの混合物、いずれから出発しても、LPG 成分炭化水素へ選択的に転化させることができた。また、希釈ガスとして窒素の代わりに部分的に水蒸気を用いたときには DME 転化率は減少した。