

## [Research Note]

## Shape-selective Methylation of 4-Methylbiphenyl to 4,4'-Dimethylbiphenyl with Supercritical Methanol over Zeolite Catalysts

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The applicability of supercritical methanol was investigated to the selective para methylation of 4-methylbiphenyl to produce 4,4'-dimethylbiphenyl, which has recently attracted much attention as a valuable monomer of thermotropic liquid crystals, engineering plastics and others. The effects of the catalysts, temperature, pressure, reaction time, initial molar ratio of methanol to 4-methylbiphenyl and initial weight ratio of catalyst to 4-methylbiphenyl were evaluated using a batch-type reactor. The combination of supercritical methanol with SAPO-11 catalyst gave an excellent product selectivity of 70-85% of 4,4'-dimethylbiphenyl at 300°C, 14-16 MPa, 0.5 h reaction time, 15-20 initial molar ratio of methanol to 4-methylbiphenyl and 0.4-0.6 initial weight ratio of catalyst to 4-methylbiphenyl. Comparing with supercritical and gaseous methanol, the selectivity of 4,4'-dimethylbiphenyl in the supercritical phase was 1.5-3.4 times higher than that in the gas phase at the same conversion of 20-50% of 4-methylbiphenyl. The methylation almost stopped around 1 h due to coke deposition on the catalyst surface.

**Keywords**

Supercritical methanol, Shape selectivity, Methylation, Zeolite catalyst, Dimethylbiphenyl

**1. Introduction**

The development of new synthesis methods for symmetrically methylated compounds is desirable in many industrial fields, because of the wide applications as monomers of liquid crystal polymers and others<sup>1)</sup>. In particular, the selective synthesis of 4,4'-dimethylbiphenyl (4,4'-DMBP) is important as a valuable monomer for the production of advanced polymeric materials such as thermotropic liquid crystals and heat-resistant polymers. 4,4'-DMBP is also a more desirable starting material than 4,4'-diisopropylbiphenyl for the production of 4,4'-biphenyldicarboxylic acid, because the oxidation of 4,4'-DMBP to the corresponding carboxylic acid proceeds with high yield under mild conditions and avoids carbon loss<sup>4)</sup>. The product selectivity for 4,4'-diisopropylbiphenyl is about 90%<sup>2)</sup>, whereas 4,4'-DMBP is difficult to selectively synthesize from biphenyl or 4-methylbiphenyl (4-MBP) and methanol over a zeolite catalyst. Methylation of biphenyl with methanol over ZSM-5, Y-type zeolite and mordenite achieved a selectivity of less than 15%<sup>3)</sup>. Use of a modified phosphate ZSM-5 for the 4-MBP

methylation found improved para selectivity, but still less than 50%<sup>4)</sup>.

Supercritical methanol above the critical temperature (239°C) and critical pressure (8.1 MPa) shows strong reactivity for many types of reactions such as esterification of polyethylene terephthalate for chemical recycling of PET (poly(ethylene terephthalate)) bottles<sup>5)</sup>, and transesterification of triglycerides to methylesters for the conversion of waste cooking oil to biodiesel fuel<sup>6)</sup>. Recently we reported that ring methylation of hydroquinone, *N*-methylation of aniline, and *O*-methylation of phenols proceeded selectively without requiring a catalyst using supercritical methanol<sup>7)</sup>.

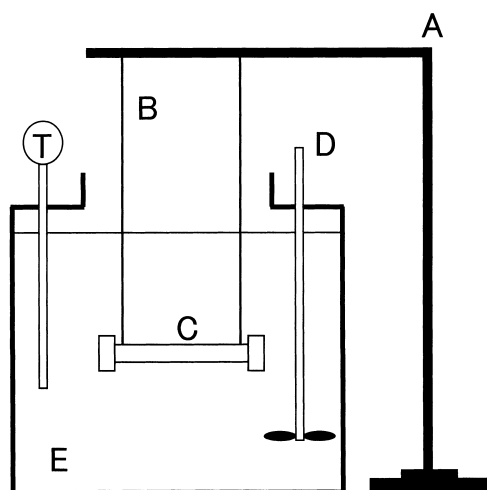
The present study investigated the use of supercritical methanol for selective methylation of 4-MBP to 4,4'-DMBP over a zeolite catalyst. The effects of catalysts, reaction temperature, reaction pressure, reaction time, initial methanol/4-MBP molar ratio and initial catalyst/4-MBP weight ratio on the 4-MBP conversion and 4,4'-DMBP selectivity were studied.

**2. Experimental Section**

A batch-type reactor was used for all experiments. The experimental apparatus is shown in **Fig. 1**. The reactor was made of 316 stainless steel and the inner

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A: Stand  
B: Hanger  
C: Reactor  
D: Agitator  
E: Molten salt bath  
T: Thermometer

Fig. 1 Experimental Apparatus

volume was 8.9-9.1 cm<sup>3</sup>. The reactor was completely immersed in a molten salt bath. The reaction temperature was considered to be equal to the temperature of the salt bath. The reaction pressure was calculated from the  $\rho$ -T relationship of methanol<sup>8)</sup>, as the reactant was assumed to be pure supercritical methanol because this was the major component in the reactor. The methanol density was determined from the weight of methanol charged into the reactor and the reactor inner volume.

The reactor was charged with 0.05-1.6 g of 4-MBP, 0.2-2.4 g of methanol and 0.03-1 g of catalyst. Then the reactor was sealed without deairing and immersed into the salt bath at 250-450°C. After 0.1-1 h, the reactor was taken out of the salt bath and cooled in water quickly to stop the reaction as soon as possible. The reactor was dried and opened, and the product and unreacted starting materials were removed from the reactor by dissolution in acetone. The products and unreacted 4-MBP were analyzed using GC (gas chromatography) and GC-MS (mass spectroscopy).

Typical GC analysis conditions were as follows: He carrier gas, DB-210 column (J&W Corp.), column temperature of 100°C increasing to 230°C at 10°C/min, and FID (hydrogen-flame ionization detector).

The catalysts were SAPO-11<sup>9),10)</sup>, ZSM-5 (CBV5020E, Zeolyst Int.), Y-type zeolite (Zeolyst Int.), mordenite (Zeolyst Int.), and silica-alumina (Nikki Chemical Corp.) dried at 600°C for 6 h. All chemicals with guaranteed grade were used as received.

The 4-MBP (reactant) conversion and product selectivity were calculated as follows:

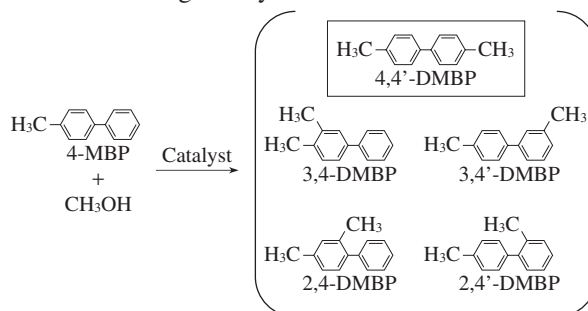
$$4\text{-MBP conversion (\%)} = \frac{([4\text{-MBP}]_0 - [4\text{-MBP}])}{[4\text{-MBP}]_0} \times 100$$

$$\text{Product selectivity (\%)} = \frac{[\text{Product}]}{[4\text{-MBP}]_0 - [4\text{-MBP}]} \times 100$$

The molecular sizes of the reactant and products were calculated by optimization of the molecular structure and the van der Waals radii of the carbon atom in the methyl group (0.2 nm), the carbon atom in the aromatic ring (0.17 nm) and the hydrogen atom (0.12 nm) using the MOPAC program.

### 3. Results and Discussion

The catalytic methylation of 4-MBP with supercritical methanol is given by



where DMBP is the abbreviation of dimethylbiphenyl.

**Table 1** presents the results of the methylation of 4-MBP with supercritical methanol over silica-alumina, ZSM-5, SAPO-11 or mordenite catalyst at 300°C, 14.7 MPa (methanol density 0.2 g/cm<sup>3</sup>), reaction time 1 h, 20 initial MeOH/4-MBP molar ratio and 0.6 initial catalyst/4-MBP weight ratio. The structural formulae of the 5 DMBP isomers are shown in the reaction formula above. SAPO-11 showed high 4,4'-DMBP selectivity but ZSM-5 and mordenite did not. The high selectivity of SAPO-11 seemed to result from the narrow pore structure and weak acidity of the catalyst. SAPO-11 showed the highest DMBP selectivity and 4,4'-DMBP composition in the DMBP isomers, and the latter exceeded 90%. The pore structure of SAPO-11 is probably optimum for the formation of DMBPs, especially 4,4'-DMBP with the slimmest molecular shape of all DMBP isomers.

The product 'others' in **Table 1** includes unknown components and the selectivity was calculated by 100 - (sum of the product selectivity except for 'others'). There were no peaks corresponding to 'others' in the GC-MS analysis, but might have been trapped in the GC column due to high boiling points. Less volatile byproducts such as polymethylbenzenes and condensed aromatic compounds are formed in the gas phase reaction of biphenyl and methanol to form 4,4'-DMBP over Y-type zeolite at 350°C and 3 MPa<sup>3)</sup>.

To investigate the reason for the high selectivity of 4,4'-DMBP production over SAPO-11, the molecular sizes of 4-MBP (reactant) and 4,4'- and 3,4'-DMBP

Table 1 Methylation of 4-MBP with Supercritical Methanol over Several Types of Zeolites

Catalyst	Pore size [nm]	4-MBP conversion [%]	Product selectivity [%]					Composition of DMBP isomers [mol%]				
			Bip	4,4'-DMBP	Other DMBPs <sup>a)</sup>	TriMBP	Others	4,4'-	3,4'-	2,4'-	3,4-	2,4-
Silica-alumina	None	6.5	6	26	27	4	37	49	12	11	12	16
ZSM-5	0.53 × 0.56	3.6	11	10	15	0	64	40	44	8	8	0
SAPO-11	0.39 × 0.63	13.7	3	67	5	1	24	93	5	1	1	0
Mordenite	0.65 × 0.70	9.0	4	25	29	3	39	46	9	12	13	20

Reaction conditions: 300°C, 14.7 MPa (methanol density 0.2 g/cm<sup>3</sup>), reaction time 1 h.

Methanol = 1.85 g, 4-MBP = 0.48 g, Catalyst = 0.29 g.

Initial MeOH/4-MBP molar ratio = 20. Initial catalyst/4-MBP weight ratio = 0.6.

Bip: Biphenyl, DMBP: Dimethylbiphenyl, TriMBP: Trimethylbiphenyl.

a) Other DMBPs are DMBP except for 4,4'-DMBP.

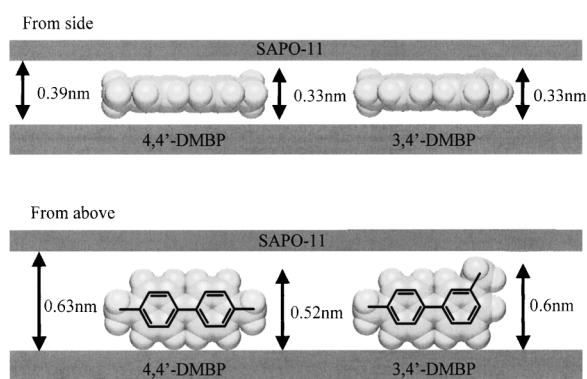
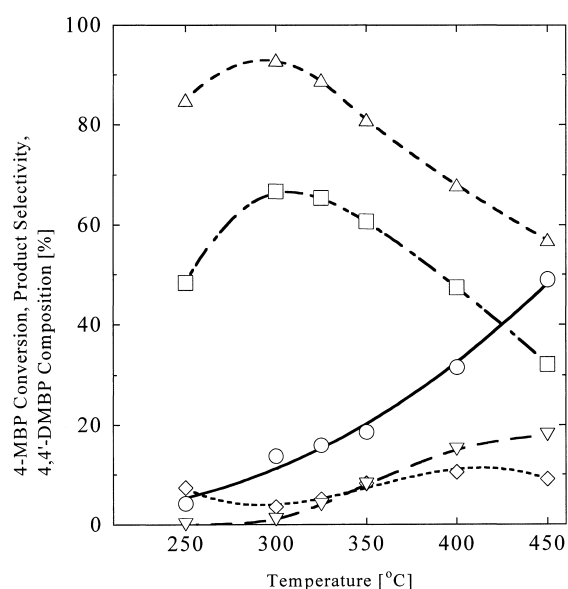


Fig. 2 Molecular Sizes of DMBP Isomers and Pore Size of SAPO-11 Calculated by the MOPAC Program

isomers (products) were calculated using the MOPAC program<sup>11)</sup> and compared with the pore size of SAPO-11. The result is illustrated in **Fig. 2**. The order of the maximum sizes was as follows: pore of SAPO-11  $\geq$  3,4'-DMBP > 4,4'-DMBP = 4-MBP. As the size of the 3,4'-DMBP molecule from the upper side was almost equal to the pore size of SAPO-11, production of 3,4'-DMBP was expected to be restrained by steric hindrance to some extent. The formation of 2,4-, 2,4'-, and 3,4-DMBPs with the same size from the upper side was also suppressed for the same reason. On the other hand, 4,4'-DMBP was slim enough to pass through the pore of SAPO-11 and so was preferentially synthesized from 4-MBP.

The present study also investigated the effect of supercritical methanol on the reaction conversion and product selectivity using SAPO-11 catalyst. **Figure 3** shows the temperature effect on 4-MBP conversion, product selectivity and 4,4'-DMBP composition in DMBP isomers using 0.2 g/cm<sup>3</sup> supercritical methanol. In this case, the pressure changed from 9.3 MPa at 250°C to 29 MPa at 450°C. The 4-MBP conversion increased with the temperature monotonously, whereas 4,4'-DMBP selectivity and composition in DMBP isomers reached maximums at around 300°C. 3,4'-

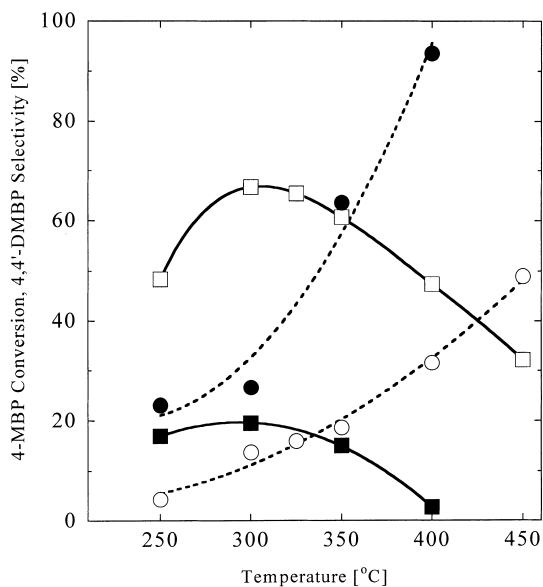


○: 4-MBP conversion, □: 4,4'-DMBP selectivity, ◇: 3,4'-DMBP selectivity, ▽: TriMBP selectivity, △: 4,4'-DMBP composition in DMBP isomers.

Fig. 3 Effect of Temperature on Methylation of 4-MBP with Supercritical Methanol over SAPO-11 at 9.3-29 MPa (0.2 g/cm<sup>3</sup> of methanol density), 1 h of Reaction Time, 20 of Initial MeOH/4-MBP Molar Ratio and 0.6 of Initial Catalyst/4-MBP Weight Ratio

DMBP selectivity increased from 300°C and reached the maximum at 400°C because 4,4'-DMBP isomerized to thermodynamically more stable 3,4'-DMBP<sup>4),12)</sup>. When the reaction temperature increased further, the trimethylbiphenyl selectivity increased gradually. These results indicate that successive reaction of 4-MBP  $\rightarrow$  4,4'-DMBP  $\rightarrow$  3,4'-DMBP  $\rightarrow$  TriMBP occurred with the increase in the temperature. In the gas-phase methylation from 4-MBP to 4,4'-DMBP over modified phosphate ZSM-5, the appropriate reaction temperature is about 300°C to avoid side reactions<sup>4)</sup>.

**Figure 4** compares 4-MBP conversion and 4,4'-



○: 4-MBP conversion at 0.2 g/cm<sup>3</sup>, □: 4,4'-DMBP selectivity at 0.2 g/cm<sup>3</sup>, ●: 4-MBP conversion at 0.02 g/cm<sup>3</sup>, ■: 4,4'-DMBP selectivity at 0.02 g/cm<sup>3</sup>.

Fig. 4 Comparison of 4-MBP Conversion and 4,4'-DMBP Selectivity in Supercritical Methanol (9.3-29 MPa, 0.2 g/cm<sup>3</sup> of methanol density) with Those in Gaseous Methanol (2.8-3.3 MPa, 0.02 g/cm<sup>3</sup> of methanol density) over SAPO-11 at 1 h, 20 of Initial MeOH/4-MBP Molar Ratio and 0.6 of Initial Catalyst/4-MBP Weight Ratio

DMBP selectivity in supercritical methanol phase and in gaseous methanol. 4-MBP conversion in the gas phase was higher than that in the supercritical phase, whereas 4,4'-DMBP selectivity showed the opposite behavior. The maximum 4,4'-DMBP selectivity in the supercritical phase was 67%, 3.4 times higher than that in the gas phase at the same temperature. The maximum 4,4'-DMBP composition in DMBP isomers in the supercritical phase was 93%, 4.8 times higher than that in the gas phase.

Figure 5 shows the relationship between 4-MBP conversion and 4,4'-DMBP selectivity in the supercritical and gas phases. The experimental data were the same as those shown in Fig. 4. The 4,4'-DMBP selectivity in the supercritical phase was much higher than that in the gas phase, especially in the low 4-MBP conversion region. For example, supercritical methanol achieved three times higher selectivity than gaseous methanol at the same conversion of 25%, over SAPO-11 catalyst.

Zeolites including SAPO-11 have acid sites on both the external and internal surfaces of the catalyst. SAPO-11 has a surface area of 240 m<sup>2</sup>/g, so the internal surface area is probably much greater than the external surface area. Therefore, the number of acid sites on the internal surface can be assumed to be much larger

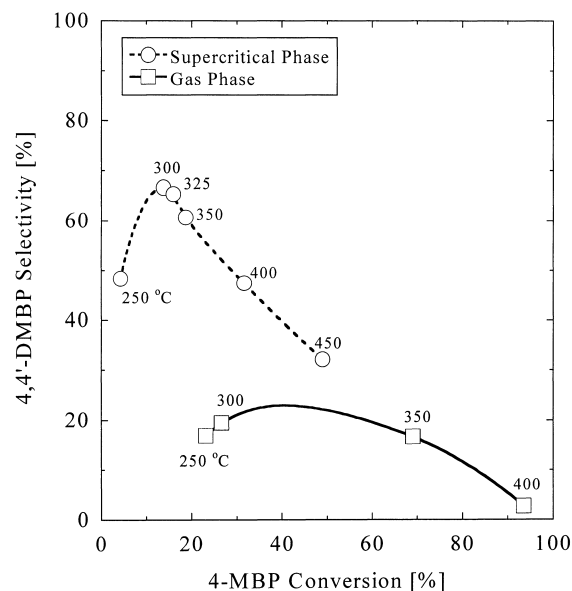
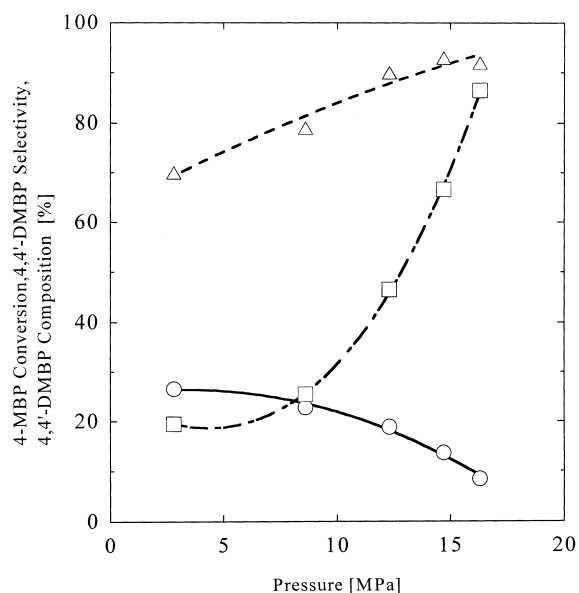


Fig. 5 Relation between 4-MBP Conversion and 4,4'-DMBP Selectivity in Supercritical and Gas Phases over SAPO-11 at 250-450°C, 1 h, 20 of Initial MeOH/4-MBP Molar Ratio and 0.6 of Initial Catalyst/4-MBP Weight Ratio

than that on the external surface. Furthermore, both internal and external acid sites are likely to be deactivated by coke at the same rate, and the acid sites were deactivated by supercritical methanol more rapidly than by gaseous methanol because the former has a higher methanol density.

Based on these three assumptions, there are two possible mechanisms to explain the high product selectivity of 4,4'-DMBP in supercritical methanol. The first mechanism is as follows. In a short reaction time, the number of the remaining active acid sites on the external surface greatly decreases, whereas the number on the internal surface does not decrease so much in the supercritical methanol phase because the total number of the acid sites is quite different between internal and external surfaces. As a result, 4-MBP methylation proceeds preferentially at the internal acid sites which controlled the product shape to form the para isomers of DMBPs. In contrast, the external acid sites are not deactivated so rapidly in the gas phase with low methanol density, so the methylation proceeds on both external and internal sites. The second mechanism is as follows. Supercritical methanol deposits more coke in the pores of SAPO-11 than gaseous methanol. As a result, the pore size of SAPO-11 is slightly narrowed which increases the para selectivity in supercritical methanol<sup>13</sup>. This effect would be smaller in gaseous methanol with low density.

The effect of the reaction pressure on the methylation of 4-MBP over SAPO-11 was investigated at 300°C, where the maximum selectivity of 4,4'-DMBP

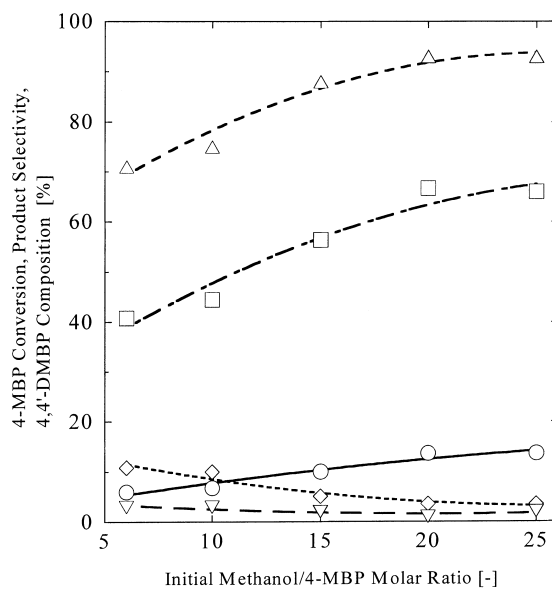


○: 4-MBP conversion, □: 4,4'-DMBP selectivity, △: 4,4'-DMBP composition in DMBP isomers.

Fig. 6 Pressure Effect on Methylation of 4-MBP over SAPO-11 at 300°C, 1 h, 20 of Initial MeOH/4-MBP Molar Ratio and 0.6 of Initial Catalyst/4-MBP Weight Ratio

was obtained. The result is shown in **Fig. 6**. 4-MBP conversion decreased with increasing pressure gradually, whereas 4,4'-DMBP selectivity and 4,4'-DMBP composition in DMBP isomers increased. These findings were probably due to the same reasons mentioned above, that high pressure caused an earlier decrease in the number of external acid sites or reduction of the pore size of SAPO-11. Furthermore, high pressure increased 4,4'-DMBP formation with the smallest activation volume among the isomers. In the supercritical region of 16.3 MPa, 4,4'-DMBP selectivity was very high and approached 90%, and 4,4'-DMBP composition in DMBP isomers was 92%. This result indicates that most products were DMBP isomers and the principal isomer was 4,4'-DMBP.

The effect of the initial MeOH/4-MBP molar ratio was investigated at 300°C and 15 MPa, at which the 4,4'-DMBP selectivity was high, as shown in **Fig. 7**. The amount of 4-MBP loaded in the reactor was changed with a constant amount of methanol. The reaction pressure was calculated from the  $p$ - $T$  relationship of methanol assuming that the reactant was pure supercritical methanol. An increase in the initial methanol ratio resulted in a gradual increase in the 4-MBP conversion and moderate increases in the 4,4'-DMBP selectivity and 4,4'-DMBP composition. On the other hand, a high methanol ratio suppressed the selectivity for 3,4'-DMBP and TriMBP. As mentioned previously, a large amount of supercritical methanol was expected to deactivate the external acid



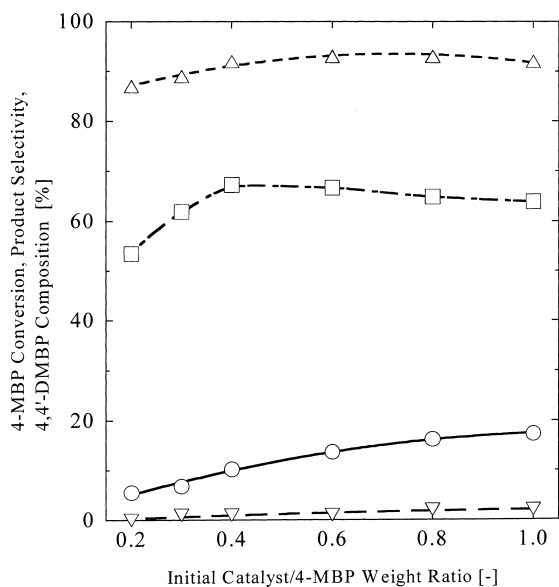
○: 4-MBP conversion, □: 4,4'-DMBP selectivity, ◇: 3,4'-DMBP selectivity, ▽: TriMBP selectivity, △: 4,4'-DMBP composition in DMBP isomers.

Fig. 7 Effect of Initial Methanol/4-MBP Molar Ratio on Methylation of 4-MBP with Supercritical Methanol over SAPO-11 at 300°C, 15 MPa, 1 h, 0.6 of Initial Catalyst/4-MBP Weight Ratio

sites earlier or narrow the catalytic pores thus favoring selective para methylation at the internal acid sites. A large excess of methanol to 4-MBP was useful to increase the 4-MBP conversion, 4,4'-DMBP selectivity and 4,4'-DMBP composition, but would increase the process costs. Judging from these two opposite factors, an initial MeOH/4-MBP molar ratio of 15-20 would be reasonable for industrial production.

**Figure 8** shows the effect of the initial catalyst/4-MBP weight ratio on methylation of 4-MBP. An increase in the ratio of SAPO-11 resulted in a slight increase in 4-MBP conversion and 4,4'-DMBP composition. However, the 4,4'-DMBP selectivity increased up to an initial catalyst/4-MBP weight ratio of 0.4 and then decreased slightly. In contrast, TriMBP selectivity gradually increased at an initial catalyst ratio of 0.4, supporting the assumption of conversion from 4,4'-DMBP to TriMBP. A large amount of catalyst did not improve the 4,4'-DMBP selectivity. The initial catalyst/4-MBP weight ratio of 0.4 was optimum for the synthesis of 4,4'-DMBP.

**Figure 9** shows the effect of the reaction time on the methylation of 4-MBP. 4-MBP conversion increased slowly until 1 h, and 4,4'-DMBP selectivity increased until 0.5 h and did not subsequently change. The increase in 4,4'-DMBP selectivity was probably due to the same reasons mentioned in **Fig. 5**. Reuse of SAPO-11, after methylation for 1 h, resulted in 4-MBP



○: 4-MBP conversion, □: 4,4'-DMBP selectivity, ▽: TriMBP selectivity, △: 4,4'-DMBP composition in DMBP isomers.

Fig. 8 Effect of Initial Catalyst/4-MBP Weight Ratio on Methylation of 4-MBP with Supercritical Methanol over SAPO-11 at 300°C, 15 MPa, 1 h and 20 of Initial MeOH/4-MBP Molar Ratio

conversion of only 2% for 1 h methylation. Therefore, the methylation had almost stopped after 1 h over SAPO-11 because of deactivation of the catalyst.

#### 4. Conclusions

The present study obtained several useful results for the shape-selective methylation of 4-MBP to 4,4'-DMBP with supercritical methanol and SAPO-11:

- (1) The optimum conditions to produce 4,4'-DMBP from 4-MBP with methanol and a zeolite catalyst were reaction temperature 300°C, pressure 14-16 MPa (methanol density 0.2-0.25 g/cm<sup>3</sup>), reaction time 0.5 h, initial MeOH/4-MBP molar ratio 15-20, initial catalyst/4-MBP weight ratio 0.4-0.6 and SAPO-11 catalyst.
- (2) Supercritical methanol increased 4,4'-DMBP selectivity and decreased 4-MBP conversion, probably by earlier deactivation of the external acid sites or decrease in the pore size of the catalyst by coke formation.
- (3) The maximum selectivity for 4,4'-DMBP was more than 85%, and 4-MBP conversion was around 10% at the same reaction condition.
- (4) The methylation almost stopped after 1 h due to deactivation of the catalyst.

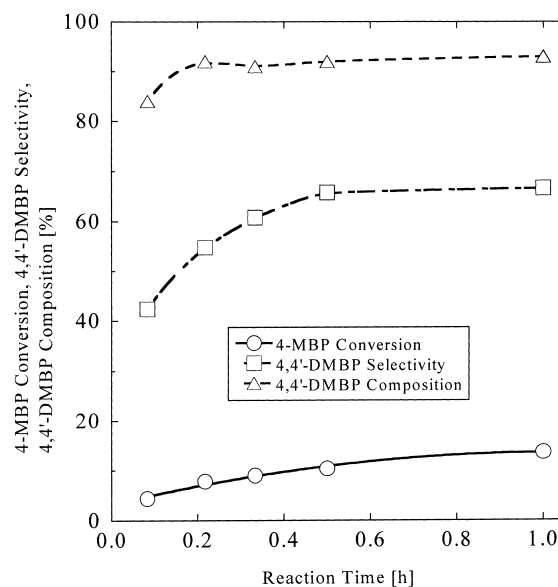


Fig. 9 Effect of Reaction Time on Methylation of 4-MBP with Supercritical Methanol over SAPO-11 at 300°C, 15 MPa, 20 of Initial MeOH/4-MBP Molar Ratio and 0.6 of Initial Catalyst/4-MBP Weight Ratio (MeOH = 1.75 g, 4-MBP = 0.46 g, Catalyst = 0.27 g)

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## 要 旨

ゼオライト触媒上での超臨界メタノールを用いた 4-メチルビフェニルから  
4,4'-ジメチルビフェニルへの形状選択的メチル化反応堀川 愛晃<sup>†1)</sup>, 内野 雄貴<sup>†1)</sup>, 七條 保治<sup>†2)</sup>, 佐古 猛<sup>†1)</sup><sup>†1)</sup> 静岡大学工学部物質工学科, 432-8561 静岡県浜松市城北 3-5-1<sup>†2)</sup> (財)化学技術戦略推進機構 超臨界流体利用技術集中共同研究体, 152-8552 東京都目黒区大岡山 2-12-1  
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最近, 液晶やエンジニアリングプラスチックの原料として注目されている 4,4'-ジメチルビフェニルの高収率合成を目的として, 4-メチルビフェニルのパラ位の選択的メチル化に対する超臨界メタノールの適用性を検討した。バッチ式反応器を用いて, 触媒の種類, 反応温度, 反応圧力, 反応時間, メタノールと 4-メチルビフェニルの仕込みのモル比, 触媒と 4-メチルビフェニルの仕込みの重量比の影響を広範囲にわたって測定した。実験結果から, 超臨界メタノールと SAPO-11 触媒を組み合わせることにより, 300℃, 14~16 MPa, 反応時間 0.5 h, メ

タノールと 4-メチルビフェニルの仕込みのモル比 15~20, 触媒と 4-メチルビフェニルの仕込みの重量比 0.4~0.6 において, 70~85% という高い 4,4'-ジメチルビフェニルの選択率が得られること, 超臨界と気相状態のメタノールを比較すると, 約 20~50% の範囲の同じ 4-メチルビフェニル転化率において, 超臨界メタノールの方が 1.5~3.4 倍高い 4,4'-ジメチルビフェニルの選択率を示すこと, 4-メチルビフェニルのメチル化は触媒表面でのコーク生成により約 1 時間で停止することがわかった。