

# REACTION ANALYSIS OF AROMATIC RING METHYLATION WITH SUPERCRITICAL METHANOL IN THE PRESENCE OF ZEOLITE CATALYST

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It has been found that industrially important methylated compound 4,4'-dimethylbiphenyl could be produced with high selectivity by the reaction of 4-methylbiphenyl with supercritical methanol over SAPO-11 catalyst. The reaction was investigated as a function of zeolite type, temperature and methanol density. In addition, we developed a unique high temperature and pressure optical cell with a diamond as an attenuated total reflection element to measure infrared spectra of reactive intermediates on catalyst surface at reaction conditions. This spectral technique can literally open the window into the industrial chemical reactors.

## INTRODUCTION

The development of new synthesis of symmetrically methylated compounds is important in many industrial fields, because they are used widely for the monomers of advanced engineering plastics, liquid crystal polymers and others<sup>1</sup>). In particular the selective synthesis of 4,4'-dimethylbiphenyl (4,4'-DMB) as a valuable precursor for the production of advanced materials such as thermotropic liquid crystals and heat-resistant polymers is an important problem. Comparing with high selectivity of 4,4'-diisopropylbiphenyl (~90 %) formation, 4,4'-DMB is usually produced from biphenyl or 4-methylbiphenyl (4-MB) over zeolite catalysts with much smaller selectivity<sup>2</sup>). However, for future applications, 4,4'-DMB is more desirable starting material than 4,4'-diisopropylbiphenyl, because its oxidation to the corresponding carboxylic acid proceeds at mild conditions and without carbon loss.

We carried out the transesterification of polyethylene terephthalate<sup>3</sup>), N-alkylation of aniline, O-alkylation of phenols and acetal formation from acetaldehyde or ketone<sup>4</sup>). In this case, supercritical methanol had high reactivity and reasonable selectivity without any catalyst.

In this work, we investigated the possibility of the selective para-methylation of 4-MB by methanol above its critical temperature over several zeolite catalysts. The effects of temperature, methanol density, methanol to 4-MB mole ratio (MMR) and catalyst to 4-MB weight ratio (CWR) on 4,4'-DMB selectivity were also studied. In addition, we developed a unique high temperature and pressure apparatus for the attenuated total reflection (ATR)

Fourier transform (FT) infrared (IR) spectroscopy to study highly concentrated solutions and heterogeneous mixtures. It was applied to find reactive intermediates formed between supercritical methanol and zeolite catalyst at our reaction conditions.

## AROMATIC RING METHYLATION WITH SUPERCRITICAL METHANOL

All kinds of zeolites were dried at 873 K for 6 h before experiments. Then methanol, 4-MBP and zeolite catalyst were loaded into a tube bomb reactor (batch type) made of SUS 316 with inner volume about 10 cm<sup>3</sup>. It was sealed using SUS 316 plugs and quickly submerged into a salt bath kept at a desired temperature. After 1 h, the reactor was quenched in water, dried and opened. The quantitative analysis of products was performed using GC and GC-MS.

In Table 1, the results of 4-methylbiphenyl (4-MB) methylation by supercritical methanol on Silica-Alumina, HZSM-5, Mordenite or SAPO-11 catalyst are shown for comparison. At the conditions of 623 K, 1 h, methanol density of 0.2 g/cm<sup>3</sup>, MMR of 10 and CWR of 0.18, SAPO-11 gave high 4-MB conversion of 19% and 4,4'-DMB selectivity of 61%. Also, the **Table 1** Comparison of 4-MB methylation by supercritical methanol over different zeolite catalysts (623 K, 1 h, Methanol density = 0.2g/cm<sup>3</sup>, MMR=20, CWR=0.59)

### (1) Product composition

Catalyst	4-MB conv. <sup>*1</sup> (%)	4,4'-DMB			TetraMB		
		selectivity <sup>*2</sup> (%)	BP	DMB	TMB	or DEB	Others
Silica-Alumina	13.76	13.86	2.78	42.13	6.45	0.48	48.16
HZSM-5	9.74	5.84	4.76	16.53	2.07	0.14	76.50
Mordenite	22.20	13.82	1.80	50.90	6.91	0.46	39.93
SAPO-11	18.56	60.68	2.13	75.09	7.99	1.22	13.57

### (2) DMB composition

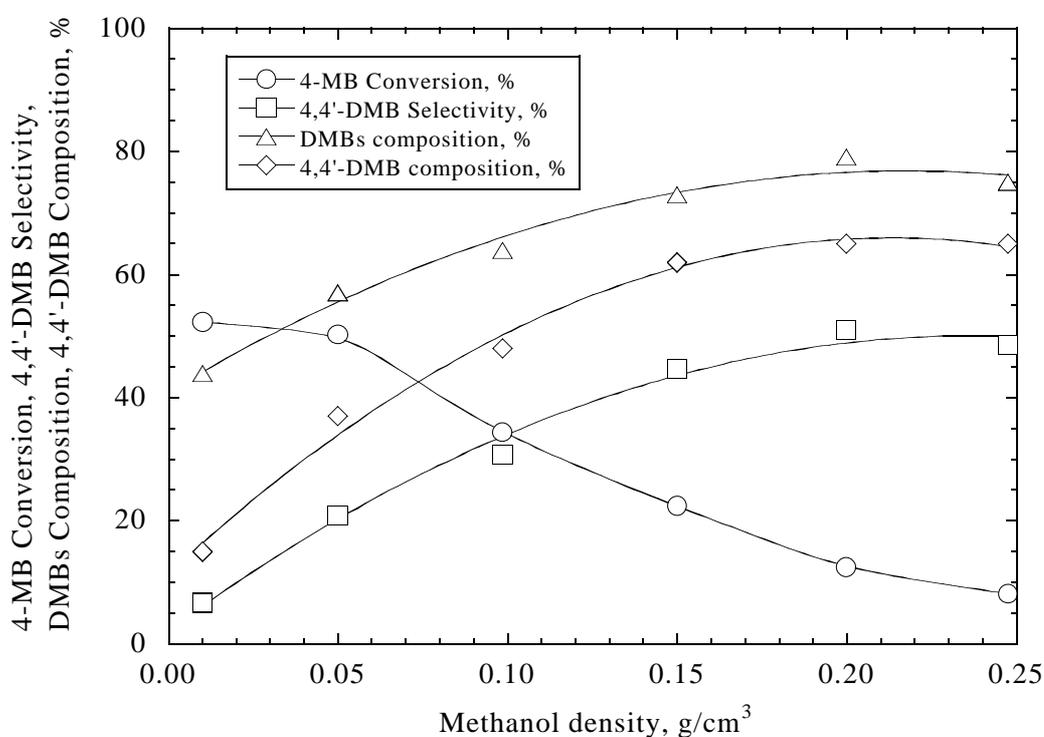
Catalyst	2,4-	3,4-	2,4'-	3,4'-	4,4'-
Silica-Alumina	24.39	17.20	15.28	10.24	32.89
HZSM-5	7.03	14.09	8.54	35.04	35.31
Mordenite	28.70	18.58	17.72	7.84	27.15
SAPO-11	1.50	5.77	1.39	10.52	80.81

$$^{*1} \text{ 4-MB conversion (\%)} = ([4\text{-MB}]_0 - [4\text{-MB}]) \times 100 / [4\text{-MB}]_0$$

$$^{*2} \text{ 4,4'-DMB selectivity (\%)} = [4,4'\text{-DMB}] \times 100 / ([4\text{-MB}]_0 - [4\text{-MB}])$$

composition of dimethylbiphenyls (DMB) in products was 75% in Table 1-(1) and that of 4,4'-dimethylbiphenyl (4,4'-DMB) in DMB the product mixture was 81% in Table 1-(2). SAPO-11 showed the highest composition among catalysts.

To explore in more details of 4-MB conversion, and 4,4'-DMB selectivity on SAPO-11, the reaction was further investigated as a function of methanol density. The result is shown in Figure 1. At 623 K, 1 h, MMR of 20, and CWR of 0.6, the change of the methanol density from 0.01 to 0.25 g/cm<sup>3</sup> led to strong decrease in 4-MB conversion from 52 to 8%. Conversely 4,4'-DMB selectivity improved from 7 to 49%. In addition, the density rise also increased the composition of 4,4'-DMB in DMB mixture from 15 to 65% as well as the composition of total DMBs in reaction mixture from 44 to 75%. From these results it is clear that methanol density plays an important role in tuning up the selectivity behavior.



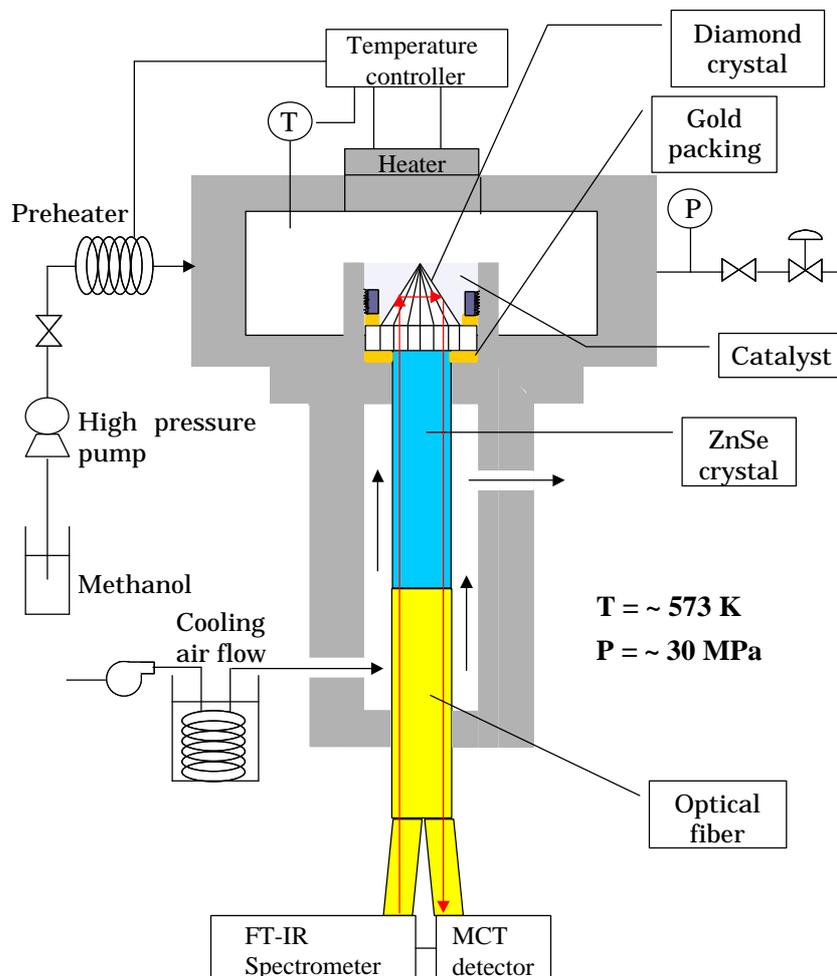
**Figure 1** The effect of methanol density on 4-MB methylation with supercritical methanol over SAPO-11

## HIGH TEMPERATURE AND PRESSURE ATR FT-IR SPECTROSCOPY

It is very interesting to understand the nature of intermolecular interactions and reactive intermediates on the surface of zeolites. Figure 2 shows a newly developed high temperature and pressure apparatus for ATR FT-IR spectroscopy. Due to a small penetration depth of IR radiation into the sample, we were able to record ATR FT-IR spectra of highly concentrated

solutions or heterogeneous mixtures at supercritical condition. The optical cell was specially built by JEOL, and it utilized the fiber-optic REMSPEC ATR probe. The key element in the optical cell was a diamond ATR crystal (hexadecagonal pyramid) used as a window. Currently the cell could withstand up to 30 MPa and 593 K.

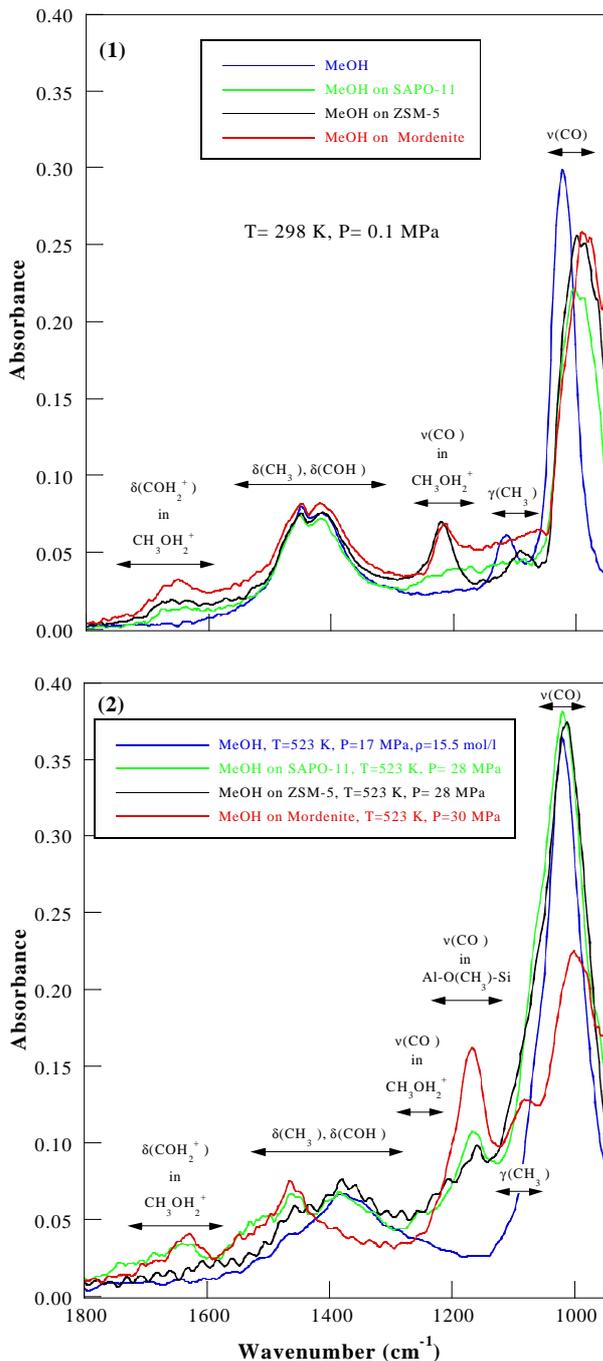
To measure ATR FT-IR spectra of methanol on zeolites, about 30 mg of catalyst powder was



**Figure 2** Optical cell of high temperature and pressure ATR FT-IR spectroscopy

strongly pressed on the ATR diamond crystal and covered by heavy SUS 316 mesh ( $5 \mu$ ) to avoid detachment. After the temperature adjustment, the baseline was measured. Then methanol was introduced into the optical cell and the spectra were recorded with  $4 \text{ cm}^{-1}$  resolution by co-adding 320 scans for each spectrum. In these experiments, due to comparatively short measurement time and small amount of catalyst (relative to methanol), no time dependence of FT-IR spectra was observed as well as no change in the baseline after the methanol evaporation.

Figure 3-(1) shows the ATR FT-IR spectra of pure methanol and methanol on Mordenite, ZSM-5 or SAPO-11 catalyst at ambient conditions. Compared to ATR spectrum of pure



**Figure 3** ATR FT-IR spectra of methanol adsorbed on the surface of different zeolites at ambient (1) and supercritical (2) conditions (297 K, 0.1 MPa for (1); 523 K, 17-30 MPa for (2))

methanol, which agreed with literature data<sup>5</sup>), the most interesting feature for zeolites saturated with liquid methanol was the appearance of new absorption bands at  $\sim 1650$  and  $1220 \text{ cm}^{-1}$ . By analogy with previous studies<sup>6,7</sup>), the band at  $\sim 1650 \text{ cm}^{-1}$  could be attributed to the  $(\text{COH}_2^+)$  vibration and  $1220 \text{ cm}^{-1}$  to the  $(\text{CO})$  vibration in methoxonium ion  $[\text{CH}_3\text{OH}_2]^+$  formed on the zeolite Brønsted acid sites. In addition, the weaker intensity of  $\sim 1650$  and  $1220 \text{ cm}^{-1}$  bands for methanol on SAPO-11 compared to Mordenite and ZSM-5 was in agreement with the known order of Brønsted acidity for these zeolites.

Figure 3-(2) represents ATR FT-IR spectra of pure and adsorbed methanol at 523 K and 17-30 MPa. Though it was difficult to see a systematic difference in the intensity of  $1650 \text{ cm}^{-1}$  band among zeolites, it was confirmed that  $[\text{CH}_3\text{OH}_2]^+$  species also existed at the high temperature. Another interesting observation was the appearance of  $1170 \text{ cm}^{-1}$  band, which could be assigned to the  $(\text{CO})$  of the surface bonded methoxy species  $[\text{Al-O}(\text{CH}_3)\text{-Si}]$ . As the temperature increased, the methoxonium ion dehydrated and changed to surface-bonded methoxy species<sup>6</sup>). Our results are the first the experimental confirmation for the existence of reactive intermediate species on zeolites at conditions relevant to possible industrial applications.

## CONCLUSION

We carried out 4-methylbiphenyl methylation with supercritical methanol over several kinds of zeolites using a batch reactor. Mordenite and ZSM-5 did not show any shape selectivity, while SAPO-11 gave excellent shape selectivity to the 4,4'-dimethylbiphenyl in the high methanol density region.

We developed the unique high temperature and pressure optical cell with the diamond as the attenuated total reflection element to measure the infrared spectra of liquid to supercritical methanol on the zeolites. We found that liquid methanol formed methoxonium ion on the zeolite Brønsted acid sites. As the temperature increased, the methoxonium ion dehydrated and changed to surface-bonded methoxy species.

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