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# Shape-selective synthesis of 4,4′-dimethyl-biphenyl over modified ZSM-5 catalysts

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## Abstract

The objective of this work is to study methylation of 4-methylbiphenyl (4-MBP) with methanol over modified ZSM-5 catalysts under fixed-bed down-flow conditions, especially the effects of zeolite structure, $SiO_2/Al_2O_3$ ratios of ZSM-5, metal oxide modification, phosphorus modification and hydrothermal treatment. The results show that, over 12-membered ring zeolites, such as HY, HM and H-Beta, there is no sign of selectivity to the target product, 4,4′-dimethylbiphenyl (4,4′-DMBP). Over 10-membered ring zeolite ZSM-5, the catalyst shows moderate selectivity to 4,4′-DMBP. A high Si/Al ratio leads to high selectivity but low catalyst activity; Both MgO modification and phosphorus modification increase the selectivity to 4,4′-DMBP, but less than 80%. Hydrothermal treatment not only increases the selectivity to 4,4′-DMBP, but also improves the stability. Treatment temperature has great effect on the activity and the selectivity in the methylation of 4-MBP with methanol. The optimal temperature range is between 400 and 550 °C. The high selectivity over modified HZSM-5 largely results from the depression of 4,4′-DMBP second reaction such as isomerization, dealkylation, as demonstrated by the reaction of 4,4′-DMBP as reactant over modified HZSM-5 and the parent zeolite.

*Keywords:* Shape selectivity; 4-Methylbiphenyl; Methylation; HZSM-5; $SiO_2/Al_2O_3$; Metal oxide modification; Phosphorus modification; Hydrothermal treatment

## 1. Introduction

Shape-selective alkylation of polycyclic hydrocarbons in preparation of symmetric intermediates such as 4,4′-dialkylbiphenyl (4,4′-DABP) or 2,6-dialkylnaphthalene (2,6-DAN), the important precursors for advanced polymer materials [1–4], has been the focus on many recent studies [4–13]. As for alkylation preparation of 4,4′-DABP, the alkylation can be carried out using either the large group like isopropyl or the small one such as ethyl and methyl groups. Like isopropylation of naphthalene and its derivates into 2,6-DAN, the alkylation of BP and its derivates can also achieve high selectivity over dealuminated mordenite, however, it is extremely difficult to selectively obtain 4,4′-dimethylbiphenyl through methylation of BP and its derivates [12,13]. Recently, some breakthrough on methylation of 4-methylbiphenyl with methanol was achieved in which Shen et al. achieved the selectivity as high as 65% over HZSM-5 modified with inorganic P compound [14,15]. However, the activity of the modified catalyst decreases with the reaction time due to the formation of coke. Therefore, the objective of this work is to find out a way to increase catalyst methylation stability, while at the same time keeping the high selectivity.

It is known that both MgO and $P_2O_5$ modification can increase the para-selectivity, and hydrothermal treatment not only increases the para-selectivity, but also improves the stability [16] in alkylation of aromatics. Generally, the structure and the acid of catalyst are thought to be the main reasons that affect the selectivity. With these encouraging findings and knowledge, in this paper we further investigated the methylation of 4-MBP with methanol over modified ZSM-5 catalysts and correlated the physical properties with catalytic reaction.

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## 2. Experimental

### 2.1. Preparation of the samples

ZSM-5 samples CBV5020E ($SiO_2/Al_2O_3$ ratio: 50) and CBV5014 (50), and HY sample CBV740 (40) were obtained from Zeolyst Int., ZSM-5 samples, CBV8020 (80) and CBV1502 (150), and $NH_4M$ sample CBV30A (38) from PQ Corp. All the samples were supplied in proton-form or ammonium-form, and were activated before the catalytic test.

The modified samples of CBV5014 (ZSM-5, H-form) with metal nitrate by an impregnation method are abbreviated as M-CBV (x) (where M = Mg, Ca, Sr, Ba and Zn, x is the weight percentage of MO based on that of HZSM-5). In a typical preparation method for Mg-CBV(5.6), 3 g HZSM-5 powder was added into 20 ml aqueous solution containing 1.101 g magnesium nitrate with magnetic stirring for 15 min at room temperature. The slurry was then put into oven (120 °C) and dried overnight, and then calcined at 450 °C for 5 h.

CBV8020 (ZSM-5, H-form) was modified with tri-phenyl phosphate [$Ph_3PO$] and ammonium hydrogen phosphate [$(NH_4)_2HPO_4$], by impregnation method; the obtained samples are abbreviated as TPP-CBV(x) and AHP-CBV(x), respectively, where x in the parenthesis indicates the weight percentage of P on the basis of ZSM-5.

Hydrothermal treatment was conducted in a quartz reactor. In a typical processing, 3 g zeolite (20–40 mesh) was placed in the middle of reactor tube (ID 3 cm). Before treatment, the furnace was heated up to 450 °C at a rate of 15 °C/min and kept 1 h, then 100% water vapor (0.1 MPa) was fed at a rate of 1 g $H_2O$/g zeolite/h through a syringe pump into furnace at 500 °C for 6 h. Prior to reaction, the samples were calcined at 450 °C for 5 h. The samples from the hydrothermal treatment were abbreviated as HT-CBV and the samples from the hydrothermal treatment plus HCl leaching were abbreviated as HCl-HT-CBV.

### 2.2. Characterization of the samples

The sample acidic property was measured by temperature-programmed desorption, TPD, of amonia on Autosorb 2910 apparatus. A certain amount of sample (typically 0.20 g) was put into sample tube and degassed, and saturated with amonia vapor at 150 °C. The desorption of amonia was recorded by TCD from 150 to 550 °C. BET sorption of $N_2$ was measured on Autosorb-1 apparatus. The samples were outgassed at 250 °C prior to measure catalyst surface areas and total pore volumes. Micropore and mesopore volumes were calculated using the *t*-plot method.

### 2.3. Catalytic test

Methylation of 4-methylbiphenyl was carried out in a fixed-bed, quartz down-flow reactor. About 0.30 g catalyst is placed in between quartz beads and activated at 450 °C for 1 h, then cooled down to 300 °C. The typical reaction conditions are as follows: feed [4-methylbiphenyl:methanol: mesitylene (as a solvent) = 1:5:5 (mol ratio)], 2 ml/h; reaction temperature 300 °C; $N_2$ flow 20 ml/min. Analysis of products was carried out by GC-MS and GC with BETA DEX® 120 column (60 m × 0.25 mm). The typical analysis conditions are as follows: flow rate of carrier gas He was set up at 1.5 ml/min inside the capillary column and temperature 300 °C was used for both detector and injector. In a typical run, the GC oven temperature was ramped up from initial 145 °C at 1 °C/min to final 190 °C, and then kept at the final temperature for 15 min.

## 3. Results and discussion

### 3.1. Effect of zeolite structure

Table 1 summarizes the results on methylation of 4-MBP with methanol over different type zeolites. As shown in Table 1, zeolites with 12-membered ring, HY, HM and H-Beta, give a range of products including all the possible isomers. There is no sign of selectivity to the target product. Thus, these three zeolites were excluded from further studies. Over 10-membered ring zeolite HZSM-5, the catalyst shows moderate selectivity to 4,4′-DMBP.

### 3.2. Effects of $SiO_2/Al_2O_3$ ratios of HZSM-5

Fig. 1 shows the results of shape-selective methylation of 4-MBP with methanol over HZSM-5 with different ratios of $SiO_2/Al_2O_3$ (time on stream is 195 min). It can be seen that the conversion of 4-MBP decreases and the selectivity to

Table 1
Effect of zeolite structure on 4-MBP methylation

| Samples | Conversion (%) | Yield (%) | | | | MBP composition (%) | | | DMBP composition (%) | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | BP | MBPs | DMBPs | Others | 2– | 3– | 4– | 2,2′– | 3,3′– | 3,4′– | 4,4′– | 2,3′– | Others |
| ZSM-5[a] | 38.2 | 1.0 | 19.0 | 7.5 | 10.8 | 0.2 | 12.3 | 76.5 | 0.7 | 5.9 | 42.3 | 26.4 | 9.0 | 15.7 |
| HY | 72.1 | 3.8 | 29.5 | 13.1 | 25.8 | 2.3 | 49.1 | 48.6 | 6.0 | 14.6 | 18.8 | 9.3 | 19.2 | 32.1 |
| HM | 80.4 | 1.0 | 29.0 | 21.2 | 29.3 | 8.4 | 51.4 | 23.4 | 0.3 | 16.1 | 17.1 | 12.1 | 20.7 | 33.8 |
| H-BETA | 93.4 | 1.9 | 0.4 | 45.2 | 28.7 | 5.7 | 0 | 94.3 | 7.5 | 4.5 | 5.9 | 8.9 | 9.8 | 63.5 |

[a] CBV5020E.

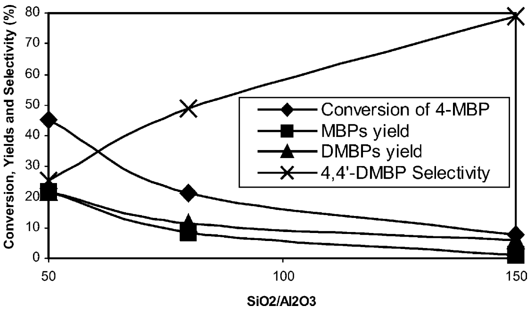

Fig. 1. Effects of $SiO_2/Al_2O_3$ ratios of HZSM-5 on methylation of 4-MBP.

4,4′-DMBP increases with an increases in the $SiO_2/Al_2O_3$ ratios of ZSM-5. On CBV1502 catalyst, when the conversion of 4-MBP is about 7.6%, the selectivity to 4,4′-DMBP is up to 79%. From the results, it can be seen that the increase of the selectivity is at the cost of the conversion of 4-MBP.

From Fig. 2, it can be seen that both acid strength and acid concentration decrease with an increase in the $SiO_2/Al_2O_3$ ratios of HZSM-5. Hence it can be concluded that the acidity is one of main reasons which affects the selectivity to 4,4′-DMBP.

In order to explore the possible reason for the high selectivity to 4,4′-DMBP over HZSM-5 with high $SiO_2/Al_2O_3$ ratios, the use of 4,4′-DMBP as reactant, instead of 4-MBP, over CBV5014, CBV8020 and CBV1502 samples was carried out under the same reaction conditions as the methylation of 4-MBP. The reaction results are listed in Table 2. As follows from Table 2 that the conversion of 4,4′-DMBP is about 85% over CBV5014 and the main products are DMBP (about 75%, from isomerization), MBP (7%, from dealkylation) and tri- and poly-methyl-biphenyl (3–4%, from alkylation). Over CBV1502 catalyst, the conversion of 4-MBP is about 52%. The main products are DMBP (47%, from isomerization), MBP (3–4%, from dealkylation) and tri- and poly-methyl-biphenyl (1–2%, from alkylation). The comparison reveals that the yields of DMBP, MBP and polymethylbiphenyl greatly decrease with an increase in the ratios of $SiO_2/Al_2O_3$. These results further demonstrate that the improving of p-selectivity over HZSM-5 with high $SiO_2/Al_2O_3$ ratio results from the restraining of the isomerization, alkylation, and dealkylation of 4,4′-DMBP over HZSM-5 zeolites.

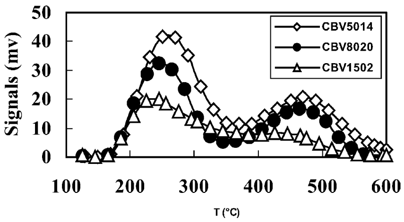

Fig. 2. TPD curves of CBV5014, CBV8020 and CBV1502.

Table 2
Reaction of 4,4′-DMBP with methanol over CBV5014, CBV8020 and CBV1502[a]

| Sample | CBV5014 | CBV8020 | CBV1502 |
|---|---|---|---|
| % 4,4′-DMBP conversion | 85.5 | 74.2 | 52.8 |
| Pdt. distribution (%, change) | | | |
| 3-MBP | 3.9 | 1.8 | 0.7 |
| 4-MBP | 3.4 | 2.8 | 3.1 |
| 3,3′-DMBP | 21.7 | 15.2 | 7.2 |
| 3,4′-DMBP | 51.1 | 49.7 | 39.1 |
| 4,4′-DMBP | 14.6 | 25.8 | 47.2 |
| Other DMBP | 2.0 | 1.1 | 1.4 |
| Tri and polymethylbiphenyl | 3.4 | 3.5 | 1.4 |

[a] Reaction at 300 °C; 4,4′-DMBP: methanol: mesitylene = 1:5:14.26 (molar ratio).

### 3.3. *Effect of metal oxide modification*

#### 3.3.1. *Methylation of 4-MBP with methanol over HZSM-5 modified with metal oxide*

Table 3 lists the results of 4-MBP methylation with methanol over HZSM-5 (CBV5014) zeolites modified with different metal oxides. It can be seen from Table 3 that over the parent zeolite HZSM-5, the selectivity of objective product 4,4′-DMBP is less than 20%. With the increasing of time of stream (TOS), the catalytic activity decreases and the selectivity to 4,4′-DMBP reaches the maximum (∼42%) because of coke formation, covering active sites over zeolite surface and narrowing the pore size. Modification of metal oxide can effectively enhance the objective selectivity. Among them, the modification of HZSM-5 with MgO (7.5) is the most effective and can improve the selectivity to 4,4′-DMBP as high as 80%. The selectivity to 4,4′-DMBP over modified HZSM-5 zeolites shows the following order: MgO>SrO∼ZnO∼CaO>BaO. From the data in Table 3, it can also be seen that the modification with metal oxide depresses the side reaction such as isomerization (the isomerization of 4-MBP into 3-MBP and the isomerization of 4,4′-DMBP into 3,3′-DMBP and 3,4′-DMBP).

The XRD spectra of Mg-CBV (x) samples show that the modification of MgO still well keeps HZSM-5 structure; nevertheless, the relative crystallinity decreases with the increasing of the loading of MgO. No crystalline MgO was detected in the XRD spectra until MgO loading is more than 15%. The XRD-undetectable MgO phase may have been highly dispersed onto the surface of HZSM-5, as evidenced by Professor Xie's group [17].

The surface area of MgO-modified HZSM-5 zeolites is listed in Table 4, as follows from this table that both the surface area and micro-porosity decrease, not surprisingly, with the increasing of the amount of magnesium oxide in the zeolites, while the meso-porosity keeps constant, revealing the main occurrence of the modification of magnesium into the micro-pore channels. TPD with $NH_3$ results also supported BET results by observing the lower strong acidity over the samples with higher amount of magnesium oxide.

Table 3
Methylation of 4-MBP with methanol over HZSM-5 zeolite modified with different metal oxides

| Samples | TOS (min) | Conversion (%) | Yield (%) | | | MBP composition (%) | | | DMBP composition (%) | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | BP | MBPs | DMBPs | 2– | 3– | 4– | 2,2′– | 3,3′– | 3,4′– | 4,4′– | 2,3′– | Others |
| CBV5014 | 75 | 64.9 | 1.3 | 48.0 | 13.7 | 1.4 | 56.4 | 42.2 | 0.0 | 21.2 | 52.4 | 13.3 | 10.2 | 2.9 |
| | 135 | 57.4 | 1.1 | 35.9 | 18.7 | 0.5 | 45.2 | 54.3 | 0.0 | 13.3 | 55.1 | 17.4 | 11.2 | 3.0 |
| | 290 | 19.7 | 0.7 | 3.4 | 15.5 | 0.0 | 4.1 | 95.9 | 0.0 | 1.5 | 44.0 | 42.6 | 11.4 | 0.5 |
| Mg-CBV (2.8) | 75 | 16.5 | 0.7 | 5.1 | 10.3 | 0.3 | 5.5 | 94.2 | 1.6 | 3.2 | 21.8 | 66.3 | 6.2 | 1.0 |
| Mg-CBV (5.6) | 45 | 8.5 | 0.9 | 3.1 | 4.5 | 0.1 | 3.1 | 96.8 | 5.5 | 0.0 | 13.3 | 77.5 | 3.8 | 0.0 |
| Mg –CBV(7.5) | 45 | 3.2 | 0.8 | 0.7 | 1.7 | 0.1 | 0.6 | 99.3 | 0.0 | 0.0 | 20.0 | 80.0 | 0.0 | 0.0 |
| Ca-CBV (1.4) | 75 | 19.8 | 0.6 | 5.2 | 13.2 | 0.1 | 6.0 | 93.9 | 0.9 | 3.3 | 30.6 | 56.4 | 8.3 | 0.6 |
| | 135 | 10.6 | 0.5 | 1.8 | 7.9 | 0.0 | 2.0 | 98.0 | 0.0 | 1.8 | 32.3 | 56.9 | 8.1 | 0.9 |
| Sr-CBV (5.6) | 75 | 17.0 | 0.7 | 3.7 | 11.9 | 0.0 | 4.3 | 95.7 | 0.4 | 2.7 | 30.4 | 57.6 | 8.3 | 0.7 |
| | 135 | 9.0 | 0.7 | 1.5 | 6.5 | 0.0 | 1.6 | 98.4 | 0.0 | 1.7 | 32.7 | 56.6 | 9.0 | 0.0 |
| Ba-CBV (5.6) | 75 | 36.4 | 0.7 | 19.9 | 14.5 | 0.2 | 23.6 | 76.2 | 2.3 | 9.1 | 42.2 | 36.7 | 7.8 | 2.1 |
| | 135 | 22.7 | 0.5 | 6.6 | 14.4 | 0.2 | 7.7 | 92.2 | 0.8 | 3.5 | 36.8 | 49.9 | 8.1 | 0.9 |
| Zn-CBV (5.6) | 75 | 17.4 | 0.7 | 6.0 | 9.9 | 0.1 | 6.6 | 93.3 | 1.5 | 2.8 | 31.7 | 55.0 | 8.2 | 0.8 |
| | 135 | 8.9 | 0.7 | 1.4 | 6.4 | 0.0 | 1.5 | 98.5 | 0.0 | 1.3 | 35.5 | 53.2 | 9.1 | 0.9 |
| Zn-CBV (11.2) | 75 | 5.3 | 0.7 | 1.1 | 3.3 | 0.1 | 1.1 | 98.8 | 0.0 | 1.5 | 31.6 | 59.3 | 7.5 | 0.0 |
| | 135 | 3.4 | 0.7 | 0.4 | 2.2 | 0.0 | 0.5 | 99.6 | 0.0 | 0.0 | 38.1 | 53.8 | 8.1 | 0.0 |

### 3.3.2. The reaction of 4,4′-DMBP with methanol over modified HZSM-5 zeolite catalysts

In order to explore the possible reason for the high selectivity to 4,4′-DMBP over MgO, ZnO-modified zeolites, the use of 4,4′-DMBP as reactant, instead of 4-MBP, over Mg-CBV (5.6) and Zn-CBV (5.6) samples was carried out under the same reaction conditions as the methylation of 4-MBP. The reaction results are listed in Table 5, together with the results over the parent zeolite. As follows from Table 5 that the conversion of 4,4′-DMBP is about 88% over CBV5014 and the main products are DMBP (about 70%, from isomerization), MBP (14%, from dealkylation) and tri- and poly-methyl-biphenyl (3–4%, from alkylation). Over Mg-CBV (5.6) catalyst, the conversion of 4-MBP is about 10%. The main products are DMBP (8%, from isomerization), MBP (1–2%, from dealkylation) and tri- and poly-methyl-biphenyl (about 0.5%, from alkylation). The comparison reveals that the yields of DMBP, MBP and polymethylbiphenyl greatly decrease after the modification, similar trend was found over Zn-CBV (5.6). These results further demonstrate that the improving of p-selectivity over the modified ZSM-5 results from the restraining of the isomerization, alkylation, and dealkylation of 4,4′-DMBP over HZSM-5 zeolites.

Table 4
Properties of MgO- or $P_2O_5$-modified HZSM-5 samples[a]

| Sample ID | Surface area ($m^2/g$) | | | Porosity ($cm^3/g$) | | |
|---|---|---|---|---|---|---|
| | Total | Micro | Meso | Total | Micro | Meso |
| CBV5014 | 388 | 324 | 64 | 0.25 | 0.16 | 0.09 |
| Mg-CBV(1.4) | 349 | 276 | 72 | 0.24 | 0.14 | 0.10 |
| Mg-CBV(2.8) | 317 | 248 | 69 | 0.22 | 0.13 | 0.09 |
| Mg-CBV(5.6) | 285 | 228 | 57 | 0.20 | 0.12 | 0.08 |
| Zn-CBV(5.6) | 286 | 225 | 61 | 0.19 | 0.12 | 0.07 |
| CBV8020 | 400 | 327 | 73 | 0.26 | 0.16 | 0.10 |
| AHP-CBV(1.7) | 332 | 267 | 65 | 0.23 | 0.13 | 0.10 |
| TPP-CBV(4.1) | 355 | 283 | 72 | 0.24 | 0.14 | 0.10 |
| TPP-CBV(8.2) | 329 | 263 | 66 | 0.23 | 0.13 | 0.10 |

[a] ZSM-5 catalysts were analyzed in the form of granules (0.5–1.0 mm).

### 3.4. Effect of phosphorus modification

Table 6 shows the effect of phosphorus [inorganic P (AHP) and organic P (TPP)] modification on the methylation of 4-MBP with methanol over CBV8020 (the time on stream is 75 min). For the modification of AHP, the selectivity to 4,4′-DMBP increases with increase in the amount of P (from 0.9 to 2.6 wt.%). When the P weight percentage is up to 1.7%, the selectivity to 4,4′-DMBP increases to about 69%, where the conversion of 4-MBP is about 16%. Further increasing P amount to 3.5 wt.% resulted in a sharp drop of activity (only ∼2%). High amount of P eliminates not only the strong acid sites leading to the secondary reaction (isomerization, dealkylation and polyalkylation), but also the intermediate acid sites leading to the alkylation of 4-MBP, and plug the pore channels. Our results (not shown in the Table) also show that after two hours' reaction, the conversion of 4-MBP decreases only about 2.2%. This indicates that AHP-CBV (1.7) shows good stability. For the modification of TPP, the selectivity to 4,4′-DMBP increases with increasing amount of P from 2.1 to 8.2 wt.%. When the P weight percentage is up to 4.1%, the selectivity to 4,4′-DMBP increases to about 68% and the conversion of 4-MBP is about 17%. Further increasing the amount of P to 12 wt.% caused little change in the selectivity to 4,4′-DMBP, but decreased the activity drastically. From the reaction results (not shown in Table 6), it can be seen that TPP-CBV (4.1) shows good stability. The conversion of 4-MBP decreases only about 0.8% after two hours' reaction.

Table 5
Reaction of 4,4′-DMBP over HZSM-5 (CBV5014), Mg-CBV (5.6), Zn-CBV (5.6) and HT-CBV5014 catalysts under methylation conditions[a]

| Samples | HZSM-5 | Mg-CBV (5.6) | Zn-CBV (5.6) | HT-CBV5014 |
|---|---|---|---|---|
| % 4,4′-DMBP conversion | 88.0 | 10.1 | 41.4 | 20.7 |
| Product distribution (%) | | | | |
| BP | 0.2 | 0 | 0 | 0 |
| 2,2′-DMBP | 0.1 | 0 | 0 | 0 |
| 2-MBP | 0.1 | 0.1 | 0.1 | 0 |
| 3-MBP | 3.2 | 0 | 0.5 | 0 |
| 4-MBP | 10.8 | 1.5 | 2.1 | 2.0 |
| 3,3′-DMBP | 20.9 | 1.4 | 4.6 | 2.5 |
| 3,4′-DMBP | 45.4 | 6.5 | 30.1 | 12.0 |
| 4,4′-DMBP | 12.0 | 89.9 | 58.6 | 79.3 |
| 2,3′-DMBP | 0.6 | 0 | 0.2 | 0 |
| Other DMBP | 3.2 | 0 | 0.1 | 0.3 |
| Tri- and polymethylbiphenyl | 3.5 | 0.6 | 3.0 | 4.0 |

[a] Reaction at 300 °C; 4,4′-DMBP:methanol:mesitylene = 1:5:14.26 (molar ratio).

Table 6
Mehtylation of 4-MBP with methanol over HZSM-5 modified with phosphorus

| Samples | Conversion (%) | Yield (%) | | | | MBP composition (%) | | | DMBP composition (%) | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | BP | MBPs | DMBPs | Others | 2– | 3– | 4– | 2,2′– | 3,3′– | 3,4′– | 4,4′– | 2,3′– | Others |
| AHP-CBV(0.9) | 33.9 | 0.8 | 21.7 | 10.3 | 0.1 | 0.3 | 24.4 | 75.3 | 1.7 | 11.3 | 38.1 | 42.3 | 6.0 | 0.7 |
| AHP-CBV(1.7) | 16.6 | 0.6 | 6.3 | 9.5 | 0.1 | 0.1 | 6.9 | 93.0 | 1.9 | 4.4 | 18.4 | 69.3 | 5.0 | 1.0 |
| AHP-CBV(2.6) | 7.3 | 0.6 | 1.0 | 5.7 | 0.1 | 0.0 | 1.0 | 99.0 | 3.3 | 1.9 | 17.0 | 72.6 | 4.2 | 1.1 |
| AHP-CBV(3.5) | 2.2 | 0.5 | 0.2 | 1.5 | 0.0 | 0.0 | 0.2 | 99.8 | 0.0 | 0.0 | 35.3 | 58.0 | 6.7 | 0.0 |
| TPP-CBV(2.0) | 24.8 | 0.6 | 14.2 | 9.3 | 0.1 | 0.2 | 15.7 | 84.1 | 1.9 | 8.2 | 27.7 | 55.7 | 5.3 | 1.3 |
| TPP-CBV(4.1) | 17.4 | 0.6 | 8.1 | 8.5 | 0.0 | 0.1 | 8.8 | 91.2 | 1.9 | 5.3 | 20.0 | 67.9 | 4.9 | 0.0 |
| TPP-CBV(8.2) | 7.0 | 0.5 | 0.9 | 5.5 | 0.1 | 0.0 | 0.9 | 99.1 | 2.2 | 2.0 | 18.3 | 71.7 | 4.9 | 0.9 |
| TPP-CBV(12.3) | 6.0 | 0.5 | 0.7 | 4.7 | 0.1 | 0.0 | 0.7 | 99.3 | 2.4 | 1.9 | 18.8 | 71.1 | 4.7 | 1.1 |

From the above results, it can be seen that TPP-CBV (4.1) and AHP-CBV(1.7) exhibit similar activity and selectivity even though significantly different P amounts were used. This can be attributed to the different location of the phosphorus compounds on the HZSM-5 zeolite. Because of its larger size, TPP is mainly located on the external surface of HZSM-5 even with higher P content. In the case of AHP, it can easily enter the internal surface in addition to the particle external surface. This is supported by the results from BET surface area (see Table 4).

### 3.5. *Effect of hydrothermal treatment*

Fig. 3 exhibits the effect of hydrothermal treatment temperature from 300 to 600 °C on the activity and selectivity in the methylation of 4-MBP with methanol (the precursor is CBV5014). Catalytic activity in 4-MBP conversion and the isomerization and alkylation products, MBPs and DMBPs almost linearly decreases with treatment temperature, when the temperature is up to 600 °C, the 4-MBP conversion is only 2.5%. The selectivity to 4,4′-DMBP, however, increases with an increase in the hydrothermal treatment temperature, reaches the maximum at around 550 °C, and then decreases as temperature goes up to 600 °C. Therefore, the suitable hydrothermal treatment temperature is in the range of 400–550 °C. The reactivity of 4,4′-DMBP with methanol over HT-CBV5014 (hydrothermal treatment temperature is 500 °C) and CBV5014 samples was carried out under the same reaction conditions as the methylation of 4-MBP. The reaction results are listed in Table 5. The comparison reveals

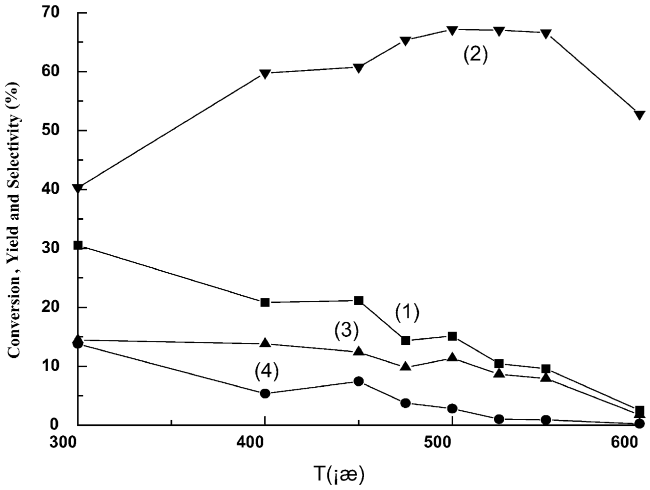

Fig. 3. Effect of hydrothermal treatment temperature on the activity and the selectivity in the methylation of 4-MBP with methanol (1) conversion of 4-MBP; (2) 4,4′-DMBP selectivity; (3) DMBPs yield; (4) MBPs yield.

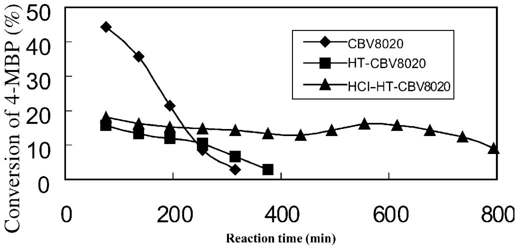

Fig. 4. Comparison of stability among CBV8020, HT-CBV8020 and HCl-HT-CBV8020.

that the yields of DMBP and MBP greatly decrease after hydrothermal treatment. These results demonstrate that the improving of p-selectivity over the hydrothermal treated HZSM-5 results from the restraining of the isomerization and dealkylation of 4,4′-DMBP over HZSM-5 zeolites.

In order to elucidate that hydrothermal treatment can improve activity stability, the methylation of 4-MBP with methanol over CBV8020, HT-CBV8020 and HCl-HT-CBV8020 catalysts was carried out. The results show that, over CBV8020, the conversion of 4-MBP decreases drastically with reaction time; when the reaction time is 255 min, the conversion of 4-MBP decreases to 3%. Both the selectivity to 4,4′-DMBP and the yield of DMBP first increases, then decreases with reaction time. Over HT-CBV8020, the selectivity to 4,4′-DMBP improves a lot, and reach about 70%; while the conversion of 4-MBP decreases with reaction time. Over HCl-HT-CBV8020, the selectivity to 4,4′-DMBP is about 65%. The conversion of 4-MBP decreases slightly with reaction time; when the reaction time is about 800 min, the conversion of 4-MBP is about 9%.

It is more evident that hydrothermal treatment improves the activity stability from Fig. 4. Hydrothermal treatment following HCl leaching not only increases the selectivity to 4,4′-DMBP, but also improves the activity stability.

## 4. Conclusion

HZSM-5 catalyst shows moderate selectivity in the methylation of 4-MBP, while HY, HM and H-Beta show no sign of selectivity. A high Si/Al ratio leads to high selectivity, but low activity. Both MgO and phosphorus modification increase the selectivity. Hydrothermal treatment following HCl leaching improves the stability. The increasing of selectivity to the target molecule mainly comes from the decreasing of acid sites and the narrowed pore channel of ZSM-5. As a result, the side reactions such as isomerization, polyalkylation and dealkylation of 4,4′-DMBP were depressed.

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