Effects of hydrothermal treatment conditions on the catalytic activity of HZSM-5 zeolites in the methylation of 4-methylbiphenyl with methanol

Xinwen Guo [a,*], Jian-Ping Shen [b], Lu Sun [b], Chunshan Song [b], and Xiangsheng Wang [a]

[a] State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian 116012, China
[b] Clean Fuels and Catalysis Program, Energy Institute and Department of Energy & Geo-Environmental Engineering, Pennsylvania State University, 209 Academic Projects Building, University Park, PA 16802, USA

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The objective of this work is to study the effects of hydrothermal treatment conditions on the methylation of 4-methylbiphenyl (4-MBP) with methanol under fixed-bed down-flow conditions. The results show that hydrothermal treatment temperature has a marked effect on the activity and selectivity in the methylation of 4-MBP with methanol. 4-MBP conversion decreases and the selectivity to 4,4′-dimethylbiphenyl (4,4′-DMBP) increases with an increase in the hydrothermal treatment temperature. The optimal temperature range is between 400 and 550 °C. After hydrothermal treatment, the catalytic selectivity to 4,4′-DMBP is up to 70%, while the 4-MBP conversion is about 12%. The high selectivity over hydrothermally treated ZSM-5 largely results from the suppression of 4,4′-DMBP secondary reactions such as isomerization and dealkylation, as demonstrated by the reaction of 4,4′-DMBP as reactant over hydrothermally treated ZSM-5 and the parent zeolite.

KEY WORDS: shape selectivity; 4-methylbiphenyl; methylation; HZSM-5; hydrothermal treatment.

1. Introduction

Shape-selective alkylation of polycyclic hydrocarbons in the 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 of many recent studies [4–13]. For the preparation of 4,4′-DABP, the alkylation can be carried out using either a large group such as isopropyl or a small one such as ethyl and methyl groups. As for the 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 obtain selectively 4,4′-dimethylbiphenyl (4,4′-DMBP) through methylation of BP and its derivates [12,13]. Recently, a breakthrough in the methylation of 4-methylbiphenyl (4-MBP) with methanol was achieved in which Shen *et al.* achieved a selectivity as high as 65% over HZSM-5 modified with an 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 the present work is to find a way to increase the catalyst methylation stability, while at the same time keeping the high selectivity.

It is known that hydrothermal treatment is an effective method to remove framework aluminum from a zeolite framework and thus tailor catalytic properties. Catalysts obtained in this way not only show improved activity stability, but also an increased *para*-selectivity [16] in the alkylation of aromatics. Thus, here we first report on the methylation of 4-MBP with methanol over hydrothermally treated HZSM-5 and correlate hydrothermal treatment with catalyst activity and stability during alkylation.

* To whom correspondence should be addressed.
E-mail: xinwenguo@yahoo.com

2. Experimental

An NH_4^+-ZSM-5 sample, CBV5014 (50), was obtained from Zeolyst Inc. and converted into the H^+-form (HZSM-5) by calcinating at 540 °C for 5 h.

Hydrothermal treatment was conducted in a quartz reactor. In a typical processing, 3 g zeolite (20–40 mesh) was placed in the middle of the reactor tube (3 cm i.d.). Before treatment, the furnace was heated to 450 °C at a rate of 15 °C/min and kept there for 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 the furnace 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.

Methylation of 4-MBP was carried out in a fixed-bed, quartz down-flow reactor. About 0.30 g catalyst was placed between quartz beads and activated at 450 °C

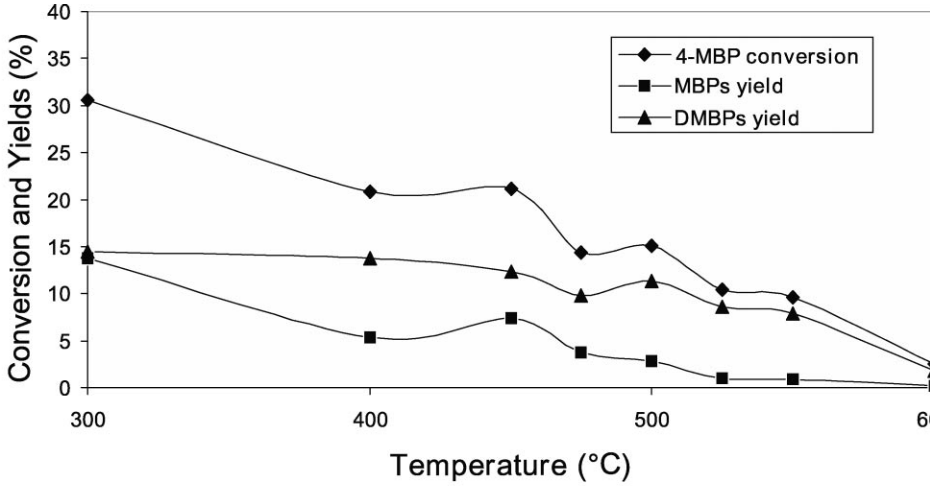

Figure 1. Effect of hydrothermal treatment temperature on the activity in the methylation of 4-MBP with methanol.

for 1 h, then cooled to 300 °C. Typical reaction conditions were as follows: feed (4-MBP : 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 a BETA DEX 120 column (60 m × 0.25 mm). Typical analysis conditions were as follows: the flow rate of He carrier gas was set at 1.5 ml/min inside the capillary column and a temperature of 300 °C was used for both detector and injector. In a typical run, the GC oven temperature was ramped up from 145 °C at 1 °C/min to 190 °C, and then kept at the final temperature for 15 min.

3. Results and discussion

3.1. *Effects of hydrothermal treatment conditions*

Figures 1 and 2 show the effect of hydrothermal treatment temperature from 300 to 600 °C on the activity and selectivity in the methylation of 4-MBP with methanol, respectively. Catalytic activity in 4-MBP conversion and the isomerization and alkylation products, MBPs and DMBPs, almost linearly decrease with treatment temperature. When the temperature is 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 a maximum at around 550 °C, and then decreases as the temperature further increases to 600 °C. Therefore, the suitable hydrothermal treatment temperature is in the range 400–550 °C.

It is known that molecular sieves will undergo framework dealumination upon steam treatment and the degree of lattice dealumination in materials such as faujasite-type zeolite from steam treatment is dependent on the temperature [17–19], *i.e.*, higher temperature usually leads to a higher degree of dealumination. The significant changes in catalytic activity and selectivity after hydrothermal treatment obviously indicated the occurrence of the removal of aluminum and structure change.

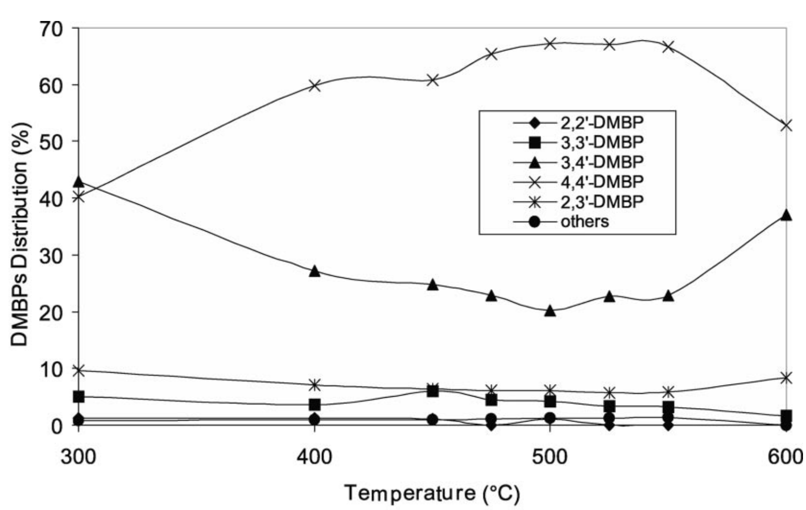

Figure 2. Effect of hydrothermal treatment temperature on the selectivity in the methylation of 4-MBP with methanol.

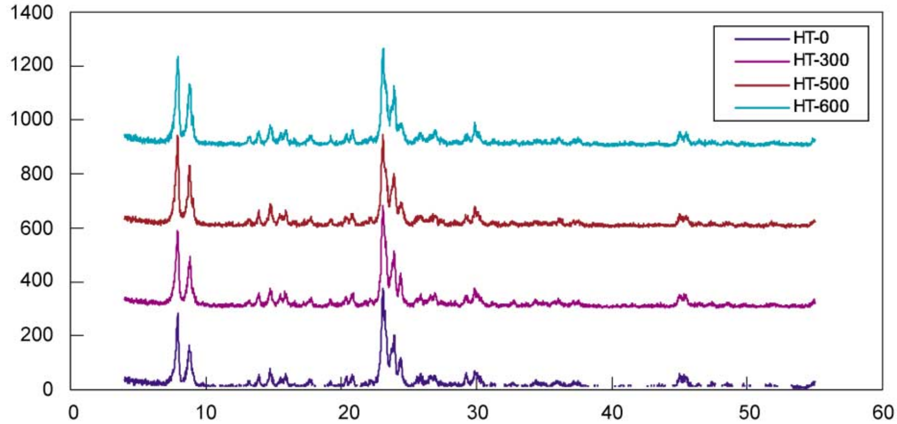

Figure 3. XRD spectra of hydrothermally treated HZSM-5 at different temperatures.

Figure 3 shows XRD spectra of HZSM-5 hydrothermally treated at different temperatures. It can be seen that the crystalline structure does not change much, although the relative strength decreases after hydrothermal treatment. Even after HZSM-5 is treated at 600 °C the framework structure still remains, which shows that the activity decrease (figure 1) after treatment at 600 °C is not due to the collapse of the framework.

Table 1 lists the BET surface properties of HZSM-5 hydrothermally treated at different temperatures and the results of elemental analysis. It can be seen that the total surface area decreases from 388 to 353 m^2/g, and micropore area decreases from 324 to 256 m^2/g, a much greater change as compared to surface area change after hydrothermal treatment. The mesopore surface area, in contrast, increases to 103 m^2/g after treatment at 500 °C from the original 64 m^2/g, then decreases to 97 m^2/g at 600 °C. As follows from the chemical analysis results, the hydrothermal treatment does not result in much of a change in bulk chemical composition, which implies that the removed Al species from the framework still remain in ZSM-5 channels, as shown by HCl leaching over CBV8020 (table 4). In correlation with catalytic results, it is found that the non-framework Al species in the channels (reducing surface area) limit the reactant access to active sites in the channels, resulting in the lower activity, as observed in figure 1. The high selectivity to 4,4′-DMBP in the range 400–550 °C might be related to the faster diffusion out of channels due to the created framework faults from hydrothermal treatment, reducing the chance of isomerization to other thermally stable isomers like 3,4′-DMBP, as evidenced in figure 2.

Figure 4 shows TPD curves of CBV5014 hydrothermally treated at different temperatures. It can be seen that hydrothermal treatment at 300 °C does not change the acid properties of CBV5014, while hydrothermal treatment at 600 °C leads to drastic decreases in the acid strength and acid concentration.

In order to explore the possible reason for the high selectivity to 4,4′-DMBP over hydrothermally treated zeolite, the use of 4,4′-DMBP as reactant, instead of 4-MBP, over hydrothermally treated samples was investigated under the same reaction conditions. The reaction results are listed in table 2 together with the results for the parent zeolite. From table 2 it can be seen that the conversion of 4,4′-DMBP is about 85% over CBV5014. The main products are DMBP (about 70%, from isomerization), MBP (9%, from dealkylation) and tri- and polymethylbiphenyl (3–4%, from alkylation). Over HT-500 catalyst the conversion of 4,4′-DMBP is about 21%. The main products are DMBP (15%, from isomerization), MBP (about 2%, from dealkylation) and tri- and polymethylbiphenyl (about 4%, from alkylation). The comparison reveals that the yields of DMBP and MBP greatly decrease after hydrothermal treatment; a similar trend was found over HT-600. The results further demonstrate that the improvement of *para*-selectivity

Table 1
BET surface properties and elemental analysis of HZSM-5 after hydrothermal treatment

Sample	Composition			Surface area (m^2/g)		
	Al_2O_3 (wt%)	SiO_2 (wt%)	SiO_2/Al_2O_3 (molar ratio)	Total	Micropore	Mesopore
HT-0	2.87	84.8	50.2	388	324	64
HT-300	2.87	88.9	52.7	375	272	102
HT-500	3.05	94.6	52.7	357	254	103
HT-600	3.12	94.2	51.3	353	256	97

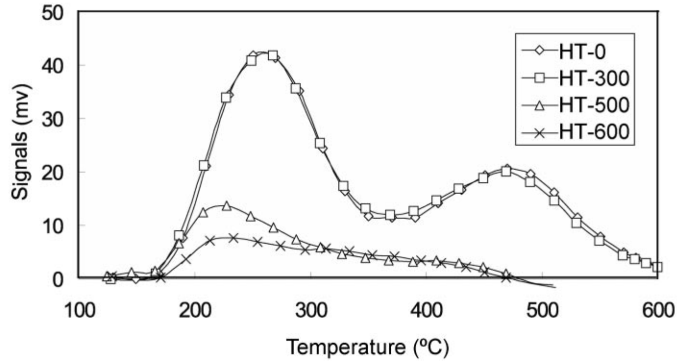

Figure 4. NH_3-TPD curves of CBV5014 hydrothermally treated at different temperatures.

over the hydrothermally treated ZSM-5 results from the restriction of the isomerization and dealkylation of 4,4′-DMBP over HZSM-5 zeolites, mainly from the isomerization.

Figures 5 and 6 show the effect of hydrothermal treatment time on the activity and selectivity of methylation of 4-MBP with methanol. It can be seen that the 4-MBP conversion decreases slightly and the selectivity to 4,4′-DMBP increases slightly with hydrothermal treatment time. When the hydrothermal treatment time is 8 h the selectivity to 4,4′-DMBP increases to about 70% while the 4-MBP conversion remains at about 12%.

Figures 7 and 8 show the effect of water vapor velocity during hydrothermal treatment on the activity and selectivity of methylation of 4-MBP with methanol. It can be seen that both the 4-MBP conversion and the selectivity to 4,4′-DMBP do not change much with water vapor velocity.

3.2. *Comparison of methylation properties of different precursors*

According to the above results, the optimum conditions for hydrothermal treatment are as follows: hydrothermal treatment temperature, 500 °C; time, 6 h; water vapor velocity, 1 g H_2O/g cat/h. Under these conditions various HZSM-5 precursors were hydrothermally treated, and their methylation properties were investigated. The results are shown in table 3. It can be seen that HZSM-5 precursors exhibit different catalytic properties; however, they exhibit similar activity and selectivity after hydrothermal treatment. This shows that hydrothermal treatment is a good method to increase the selectivity.

Table 2
Reaction of 4,4′-DMBP with methanol over HT-500 and HT-600

	HZSM-5	HT-500	HT-600
4,4′-DMBP conversion (%)	85.45	20.74	11.54
Product distribution (%, change)			
3-MBP	3.94	0	0
4-MBP	3.42	1.97	2.33
3,3′-DMBP	21.65	2.46	0.48
3,4′-DMBP	51.08	12.01	3.87
4,4′-DMBP	14.55	79.26	88.46
Other DMBP	1.95	0.34	1.42
Tri- and polymethylbiphenyl	3.40	3.97	3.44

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

3.3. *Comparison of activity stability*

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 are shown in figures 9–13. It can be seen that over HCBV8020 (figure 9) 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 increase, then decrease with reaction time. Over HT-CBV8020 (figure 10) the selectivity to 4,4′-DMBP improves much, and reaches about 70%; the conversion of 4-MBP decreases with reaction time. Over HCl-HT-CBV8020 (figure 11) the selectivity to 4,4′-DMBP is about 65%. The converion of 4-MBP decreases slightly with reaction time; when the reaction time is about 800 min the conversion of 4-MBP is about 9%. From figures 9–11 it can be seen that hydrothermal treatment increases the selectivity to 4,4′-DMBP, while the activity stability improves a little. It is more evident that hydrothermal treatment improves the activity stability from figure 12. Hydrothermal treatment following HCl leaching not only increases the selectivity to 4,4′-DMBP, but also improves the activity stability. HT-CBV8020 exhibits higher selectivity to 4,4′-DMBP than HCl-HT-CBV8020, while it exhibits lower conversion of 4-MBP than HCl-HT-CBV8020. This can be explained as follows. Hydrothermal treatment removes aluminum from the framework, but the aluminum still remains in the zeolite solid. After HCl leaching, the aluminum residing in the zeolite is removed. Table 4

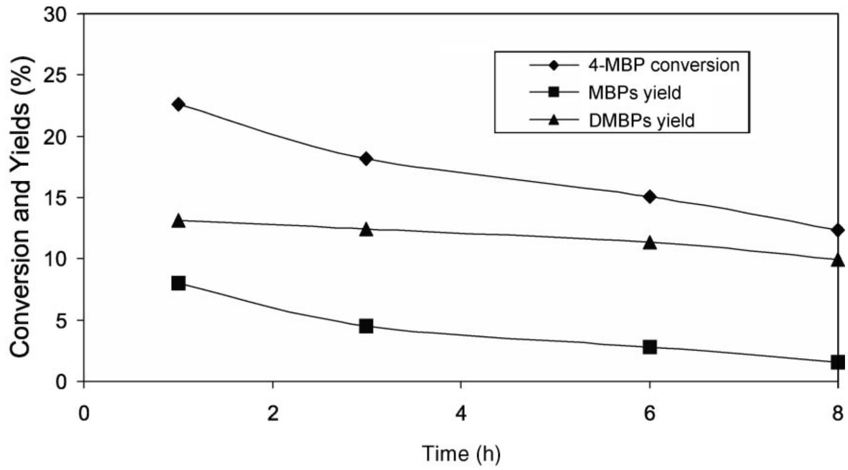

Figure 5. Effect of hydrothermal treatment time on the activity in the methylation of 4-MBP with methanol.

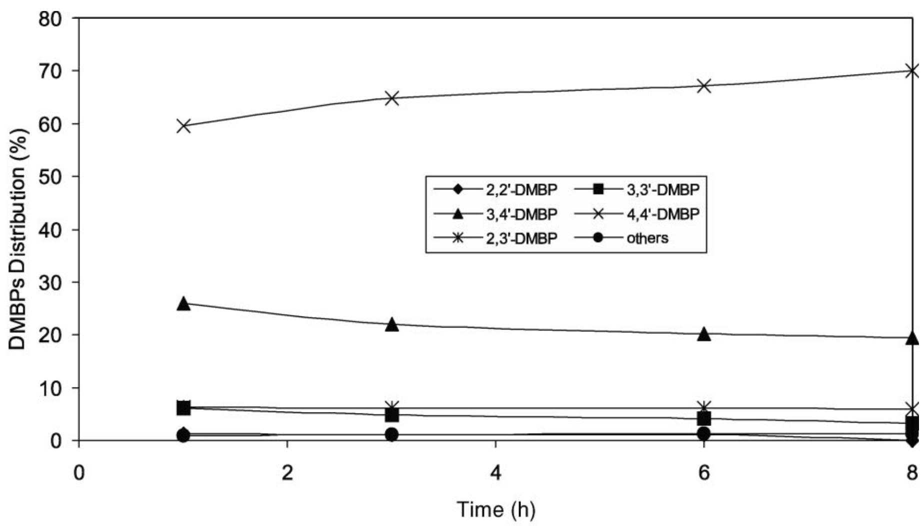

Figure 6. Effect of hydrothermal treatment time on the selectivity in the methylation of 4-MBP with methanol.

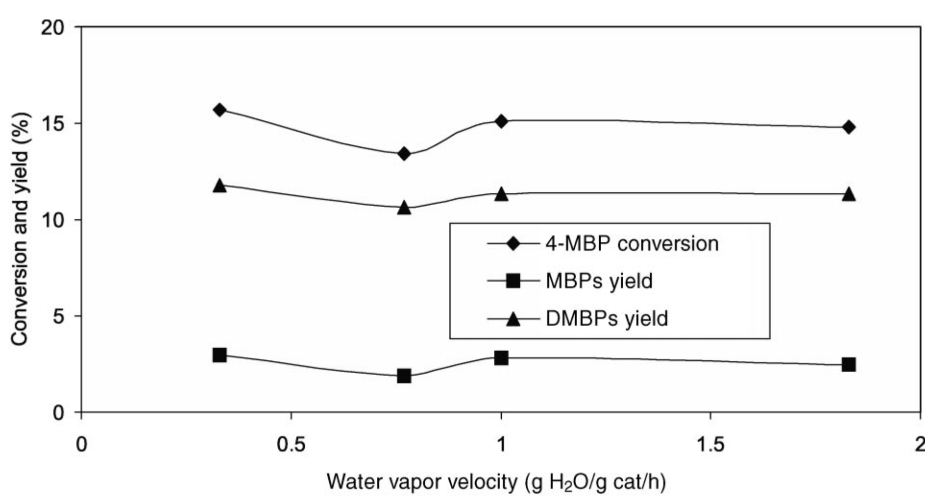

Figure 7. Effect of water vapor velocity on the activity in the methylation of 4-MBP with methanol.

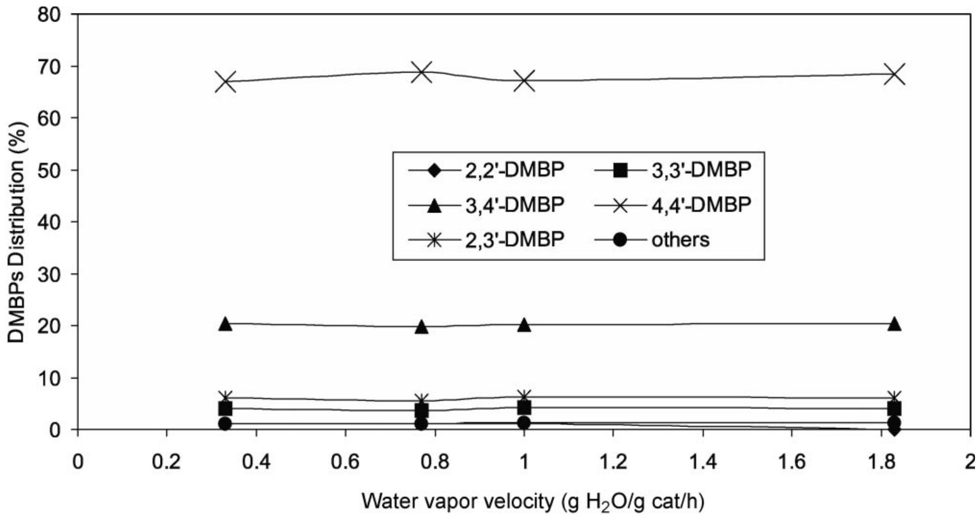

Figure 8. Effect of water vapor velocity on the selectivity in the methylation of 4-MBP with methanol.

Table 3
Shape-selective methylation over various HZSM-5 catalysts

Sample	Crystal size (μm)	Conv. of 4-MBP (%)	MBPs yield (%)	DMBPs yield (%)	4,4′-DMBP sel. (%)
CBV5014	0.2–0.3	45.13	21.56	21.54	25.30
HT-CBV5014		12.55	1.38	10.35	69.49
CBV8020	1–3	21.34	8.61	11.40	48.86
HT-CBV8020		12.00	1.80	9.43	72.85
CBV8014	–	24.02	9.28	13.00	49.31
HT-CBV8014		11.14	2.07	8.35	69.58
ZPO31055	0.1–0.2	10.69	1.91	7.81	44.43
HT-ZPO31055		11.44	1.42	9.21	66.99

Note: Reaction time is 195 min.

gives the element analysis result for CBV8020. It can be seen that the ratio of SiO_2/Al_2O_3 does not change after hydrothermal treatment, while it increases after HCl leaching. This is in agreement with reaction result.

In order to explore the importance of hydrothermal treatment and HCl leaching, CBV8020 was treated with 10% HCl at room temperature, and its catalytic properties were then investigated (figure 13). From figure 13 it can be seen that HCl treatment at room temperature neither increases the selectivity to 4,4′-DMBP nor improves the activity stability. Figure 14 shows TPD curves of CBV8020, HT-CBV8020,

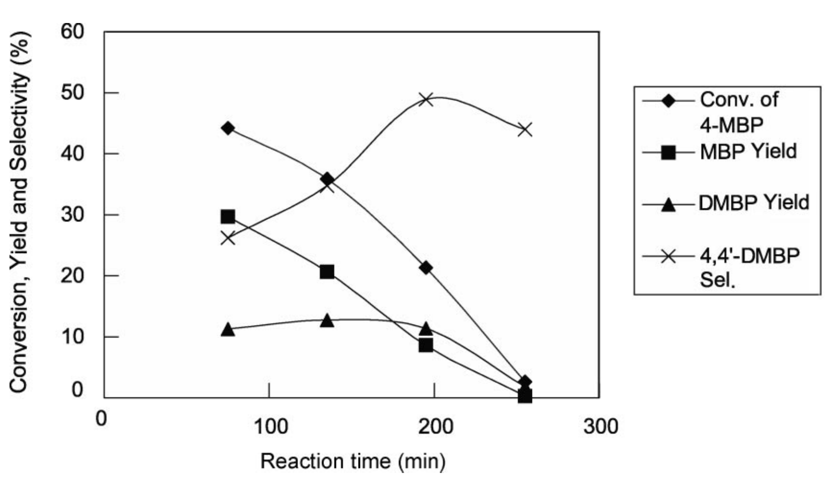

Figure 9. Methylation of 4-MBP with methanol over CBV8020.

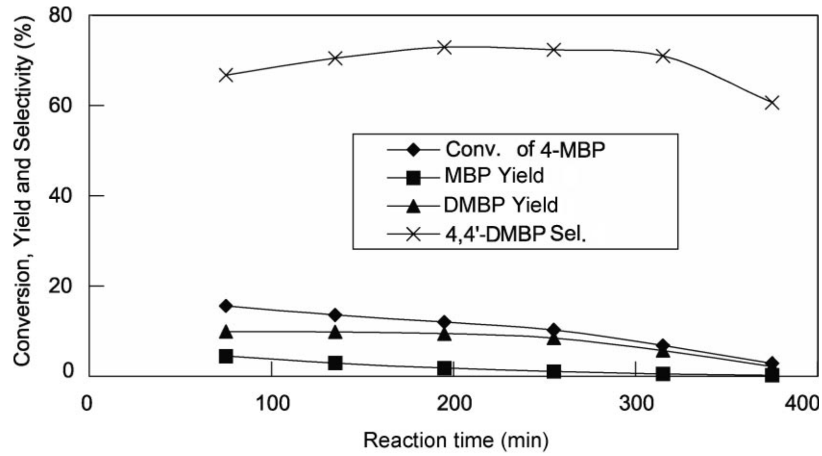

Figure 10. Methylation of 4-MBP with methanol over HT-CBV8020.

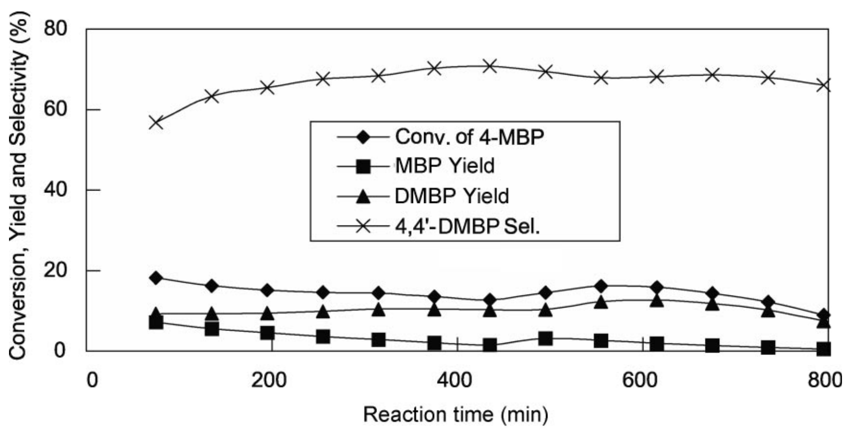

Figure 11. Methylation of 4-MBP with methanol over HCl-HT-CBV8020.

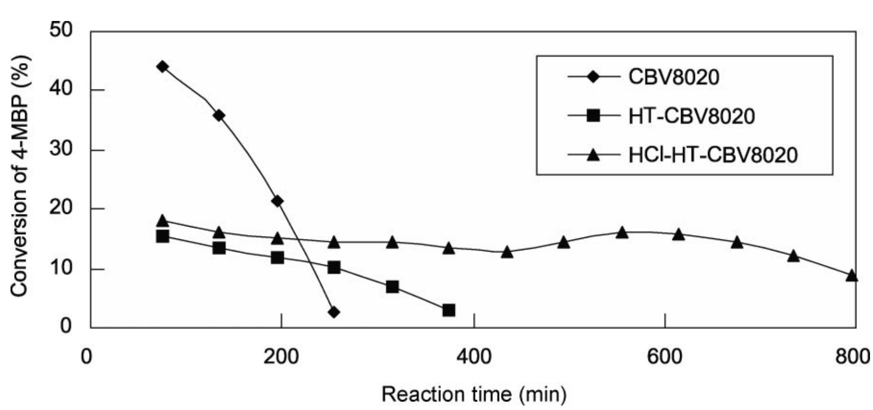

Figure 12. Comparison of activity stability of CBV8020, HT-CBV8020 and HCl-HT-CBV8020.

Table 4
Elemental analysis of CBV8020, HT-CBV8020 and HCl-HT-CBV8020

Sample	Al_2O_3 (wt%)	SiO_2 (wt%)	SiO_2/Al_2O_3 (molar ratio)
CBV8020	1.88	85.5	77.3
HT-CBV8020	1.92	87.2	77.2
HCl-HT-CBV8020	1.30	84.3	110.2

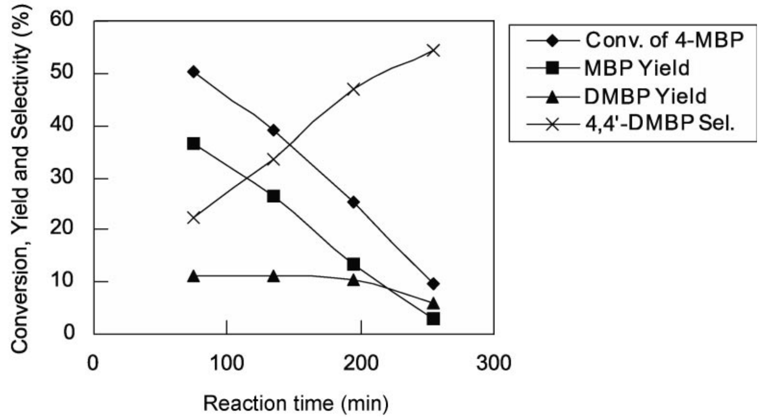

Figure 13. Methylation of 4-MBP with methanol over CBV8020 treated with 10% HCl at room temperature.

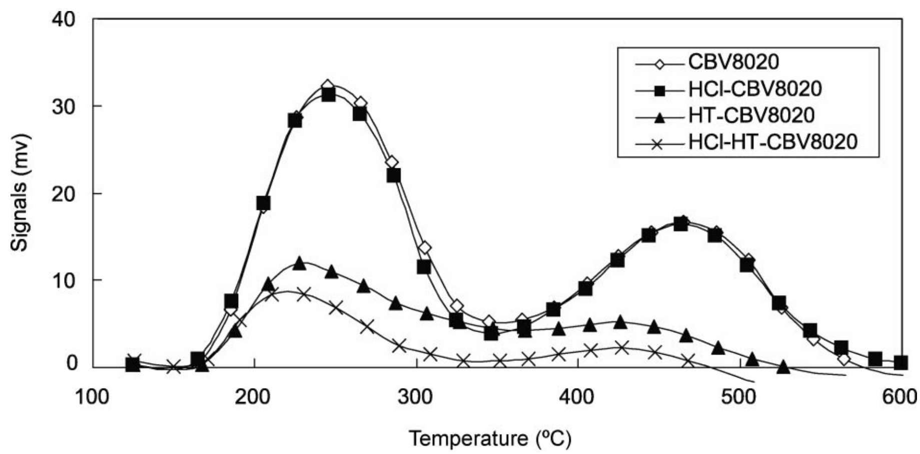

Figure 14. TPD curves of CBV8020, HT-CBV8020, HCl-HT-CBV8020 and HCl-CBV8020.

HCl-HT-CBV8020 and HCl-CBV8020. It can be seen that the treatment with HCl at room temperature does not change the acid properties of CBV8020, while hydrothermal treatment at 500 °C decreases both the acid strength and acid concentration.

4. Conclusion

Hydrothermal treatment removes the framework aluminum and decreases the acid sites. This makes the activity decrease and the selectivity to 4,4′-DMBP increase. The key factor is hydrothermal treatment temperature. The optimum temperature range is between 400 and 550 °C. Hydrothermal treatment following HCl leaching improves the activity stability.

Acknowledgments

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