Shape-selective synthesis of 4,4′-dimethylbiphenyl. 1. Methylation of 4-methylbiphenyl over modified zeolite catalysts

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Methylation of 4-methylbiphenyl with methanol was carried out using zeolites HY, HM, and HZSM-5 as catalysts under fixed-bed down-flow conditions. HY and HM display no shape selectivity, but HZSM-5 shows moderate selectivity to the target product, 4,4′-dimethylbiphenyl (4,4′-DMBP) under proper reaction conditions. Modification of the surface of HZSM-5 zeolite can improve the selectivity to 4,4′-DMBP, especially the simultaneous modification of external and internal surface with inorganic P compound. The selectivity to 4,4′-DMBP can be increased to as high as 65% over the HZSM-5 modified with a small amount of ammonium hydrogen phosphate.

Keywords: shape selectivity, 4-methylbiphenyl, methylation, zeolite, modification

1. Introduction

Shape-selective alkylation of polycyclic hydrocarbons has been the focus of many recent studies [1–10] for synthesizing the symmetric intermediates such as 4,4′-dialkylbiphenyl or 2,6-dialkylnaphthalene which are important monomer precursors for advanced polymer materials [10–13]. The challenge is to control the shape selectivity to obtain the target linear product among many isomers, 10 for dialkylnaphthalene and 12 for dialkylbiphenyl. Much research has focused on the isopropylation by which it is relatively easier to get higher selectivity because the steric hindrance of the large group can reduce the formation of the undesired isomers. For example, our previous work [4] revealed that, as the key parameter for shape selectivity in the isopropylation of naphthalene over zeolite, the ratio of 2,6-/2,7-diisopropylnaphthalene could be increased to as high as 3.0 with dealuminated mordenite under certain conditions. Similarly, for the isopropylation of biphenyl, Sugi et al. [6] reported above 90% selectivity to 4,4′-diisopropylbiphenyl. Properly modified mordenite catalysts can give over 85% selectivity to 4,4′-diisopropylbiphenyl [3,13]. However, from the viewpoint of practical application for making monomers, the corresponding methylated linear products should be much more desirable as the starting material for oxidation, partly because of the severe conditions required for oxidation of isopropyl products and of the carbon loss.

As for the use of small alkylating agent (such as ethyl and methyl groups) for biphenyl, the results in literature show that it is extremely difficult to obtain shape selectivity to 4,4′-dialkylbiphenyl. For example, Sugi et al. [8] reported that the ethylation of biphenyl over the highly dealuminated mordenite (Si/Al = 110) gives rather low selectivity for *para*-substituted biphenyl. More recently, Brechtelsbaur and Emig [9] examined methylation of biphenyl with methanol over HY, HM, and HZSM-5 in a batch reactor. They reported that HZSM-5 zeolites showed no activity and no selectivity for biphenyl methylation with methanol, while HY and HM zeolites exhibited activity but low selectivity. They also examined transmethylation of biphenyl using bulky compounds such as polymethylbenzenes as alkylating agents in order to increase the shape selectivity of HY to 4- and 4,4′-isomers.

It appears from the literature results up to now that the shape-selective methylation of biphenyl, although preferable, is very difficult. However, we were motivated by the hope for shape-selective methylation of biphenyl with methanol over zeolites with certain structural and surface characteristics. Therefore, we examined the effects of zeolite structure and reaction conditions on methylation of 4-methylbiphenyl (4-MBP) into 4,4′-dimethylbiphenyl (4,4′-DIBP), and explored ways for improving 4,4′-DIBP selectivity by surface modification. This work led us to identify methods for making highly shape-selective and promising methylation catalysts.

2. Experimental

The ZSM-5 sample (CBV5020E) was obtained from Zeolyst Int., the HY sample (CBV740) was purchased from Zeolyst Int., and the NH_4M sample (CBV30A) from PQ Corp. All the samples were supplied in proton-form or ammonium-form, and were activated before the catalytic test.

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ZSM-5 was further modified with P compounds, triphenyl phosphate [$P(Ph)_3O$] and ammonium hydrogen phosphate [$(NH_4)_2HPO_4$], by an impregnation method. The obtained samples are abbreviated as TPP-CBV(8.2) and AHP-CBV(2.6). The P weight percentage indicated in parentheses is based on ZSM-5.

Methylation of 4-methylbiphenyl was carried out in a fixed-bed, quartz 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 = 1 : 5 : 5 (mol ratio), reaction temperature 300 °C, N_2 flow 20 ml/min. Analysis of products was carried out by GC-MS and GC.

3. Results and discussion

Due to the product complexity from biphenyl alkylation, it is necessary here to mention the setup of the analysis system. Not all the GC columns can resolve the important isomers encountered in the methylation. Different kinds of GC columns were first tested and a good resolution was found for methyl and dimethyl biphenyl isomers over a DB-17 column under specific conditions, as shown in figure 1. The typical analysis conditions are as follows: He flow 1.5 ml/min inside the capillary column, 300 °C for both detector and injector, the initial GC oven temperature 145 °C, the ramp 1 °C/min to final 190 °C, and then kept at the final temperature for 10 min.

4-MBP methylation over 12-membered ring zeolites HY and HM, shown in table 1, gives a whole range of products including all the possible isomers. The products are very complex, and there is no sign of selectivity to the target product. Thus, these two zeolites were excluded from further studies.

Figure 2 shows the typical results for methylation of 4-MBP over unmodified HZSM-5, which also indicates quick deactivation. In the initial stage the isomerization of 4-MBP occurs significantly even though a high ratio of methanol to 4-MBP (5 : 1) was employed in the feed. Among MBP isomers, the main product is 3-MBP, which is in good agreement with the equilibrium. From the composition of dimethylbiphenyl (DMBP) isomers shown in figure 3, it can be seen that the distributions of thermodynamically favored product 3,4′-DMBP, and the desired symmetric compound 4,4′-DMBP are close in yields and dominant in the products, around 40%. This implies that HZSM-5 shows moderate selectivity to 4,4′-DMBP (the percentage of 3,4′-DMBP should be much higher than that of 4,4′-DMBP according to the equilibrium) under the conditions employed in this work. This observation is quite different from the literature results obtained from methylation of biphenyl in a batch reactor showing no selectivity to 4,4′-DMBP [9]. Therefore, effects of reaction conditions

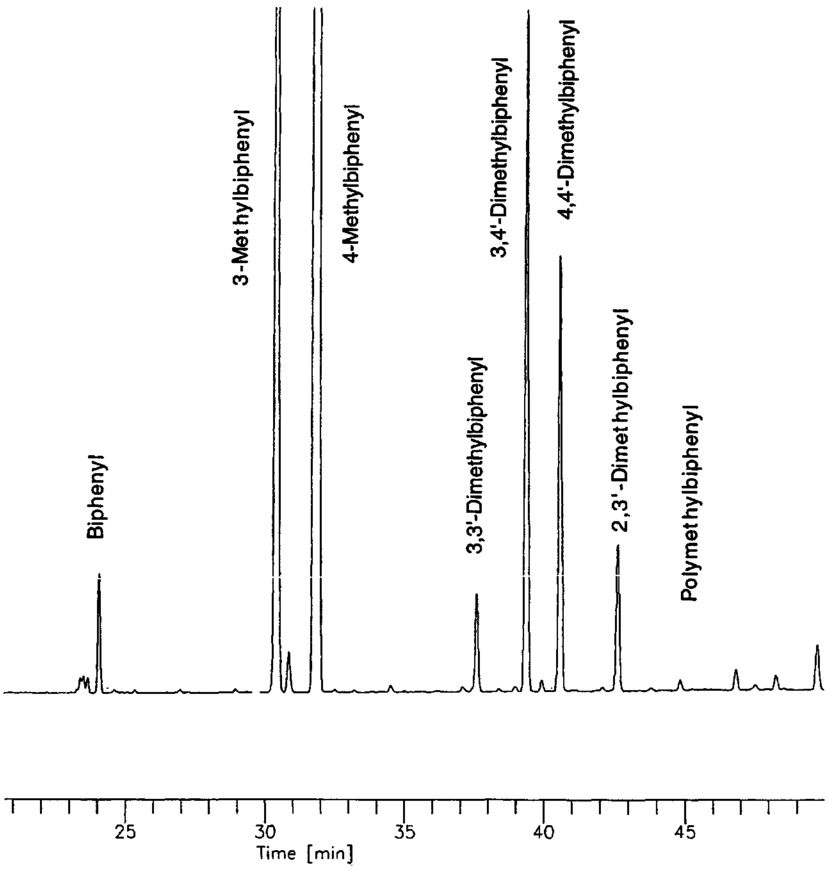

Figure 1. Capillary GC profile of biphenyl derivatives on DB-17 column.

Table 1
Effects of zeolite type, reaction conditions and zeolite modification on 4-methylbiphenyl methylation.[a]

	TOS	Conv.	Yield (%)				MBP composition (%)			DMBP composition (%)					
	(min)	(%)	BP	MBPs	DMBPs	Others	2-	3-	4-	2,2′-	3,3′-	3,4′-	4,4′-	2,3′-	Others
Zeolite (SiO_2/Al_2O_3)															
HY(40)	60	72.11	3.76	29.50	13.10	25.75	2.30	49.10	48.60	6.03	14.58	18.78	9.31	19.24	32.06
HM(38)	63	80.44	0.96	29.04	21.16	29.28	8.37	51.38	23.37	0.33	16.07	17.06	12.05	20.70	33.79
HZSM-5(50)[b]	63	38.22	0.96	19.02	7.49	10.75	0.17	12.29	76.46	0.70	5.90	42.31	26.42	9.00	15.66
	120	19.13	0.68	3.87	14.33	0.25	0.09	4.47	95.43	0.00	1.54	42.85	37.15	10.12	8.35
HZSM-5(50), temp. (°C)[b]															
280	120	25.32	1.13	9.44	13.15	1.60	0.08	11.14	88.74	0.46	3.57	46.16	36.05	10.04	3.75
350	110	56.88	1.26	41.02	13.10	1.50	1.90	47.74	50.36	0.63	18.65	41.69	18.18	9.56	11.29
400	110	68.18	1.31	53.28	12.31	1.28	7.26	55.35	37.39	0.49	23.64	35.01	10.64	7.55	22.66
HZSM-5(50), gas flow (N_2, ml/min)[b]															
40	102	43.81	0.90	24.74	14.58	3.59	0.37	30.20	69.43	0.73	10.40	43.84	29.14	9.31	6.65
60	110	35.78	1.25	19.33	14.22	0.98	0.34	22.79	76.87	0.99	8.38	38.18	37.50	8.52	5.82
HZSM-5(50), feed (ml/h)[b]															
4.0	120	11.73	1.08	1.49	8.48	0.68	0.04	1.62	98.34	0.00	0.71	41.98	37.15	10.97	3.42
6.0	110	6.79	1.10	0.74	4.68	0.27	0.00	0.79	99.21	0.00	0.00	42.31	37.15	11.75	5.98
HZSM-5(50), modification (P, wt%)[b]															
TPP-CBV(8.2)	60	19.87	0.72	7.49	11.02	0.64	0.25	8.30	91.45	0.27	3.99	21.51	56.62	5.08	12.52
	120	15.85	0.67	4.09	10.52	0.57	0.18	4.45	95.36	0.10	3.14	24.24	60.65	5.61	6.27
AHP-CBV(2.6)	60	9.29	0.67	1.52	7.03	0.07	0.13	1.52	98.35	0.00	2.13	20.77	65.72	4.41	6.97
	120	6.93	0.69	0.93	5.26	0.05	0.09	0.90	99.01	0.00	1.52	23.76	63.50	4.56	6.65

[a] Typical reaction conditions: reaction temperature 300 °C, feed 2 ml/h, methanol : 4-MBP : mesitylene = 1 : 5 : 5 (mol), carrier gas N_2 20 ml/min, catalyst 0.30 g.

[b] The reaction over HZSM-5 and reaction conditions are the same if not specifically noted.

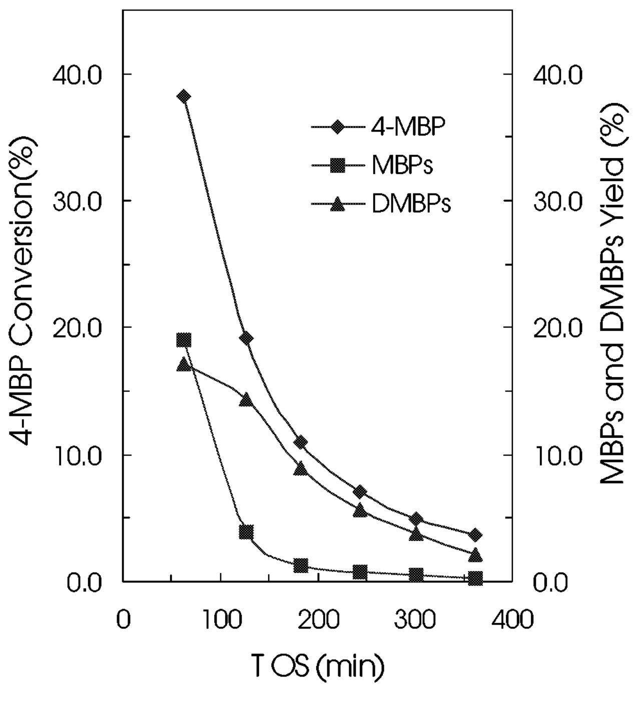

Figure 2. Conversion and yields of DMBP and MBP isomers from 4-MBP methylation over HZSM-5.

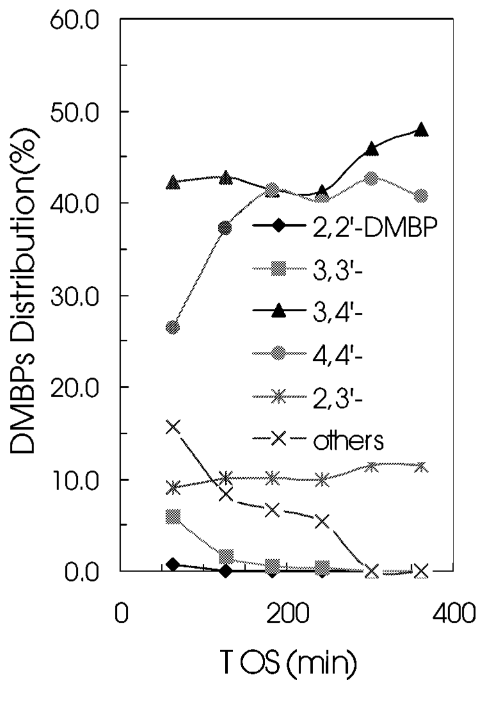

Figure 3. Distribution of DMBP isomers from 4-MBP methylation over HZSM-5.

and modification were further investigated to improve the selectivity of HZSM-5.

Table 1 shows the effects of reaction conditions on 4-MBP methylation over ZSM-5. Based on the data from tests in the reaction temperature range of 280–400 °C, it is clear that increasing temperature significantly enhances 4-MBP isomerization (from yield of 9.44% at 280 °C to 53.28% at 400 °C, respectively) since the products from alkylation changes a little, around 13. DMBP composition analysis reveals that as reaction temperature increases above 300 °C, the yield of the desired product, 4,4′-DMBP, is greatly suppressed, and the formation of 3,3′-DMBP is favored which is also the thermodynamically most favored product in terms of the equilibrium. Thus, a moderate temperature of around 300 °C is superior for selective methylation.

The use of carrier gas at flow rate of 20–60 ml/min can enhance the selectivity of 4,4′-DMBP, especially in the initial reaction stage. This may be attributed to the enhanced product removal from the surface. In other words, 4,4′-DMBP can be removed more rapidly from the surface with higher gas flow rate, thus the chance for secondary reaction of 4,4′-DMBP itself such as isomerization over the surface, can be reduced. In the later stage of methylation, 4,4′-DMBP portion reaches almost the same value regardless of gas flow rate. This is due to the quick deactivation of external surface (as can be seen from the trends in figure 2), which is mainly caused by the coverage of coke on the external surface of ZSM-5.

As shown in table 1, increasing the liquid feed flow rate decreases the conversion of 4-MBP. However, it is interesting to note that the selectivity to 4,4′-DMBP essentially remains constant in the range of feed rate examined. Thus, the optimum reaction conditions are as follows: reaction temperature 300 °C, carrier gas flow around 20–40 ml/min and feed flow rate of 2 ml/h. Consequently, further reactions were carried out under these conditions.

In order to improve the selectivity of the desired product, the modification of surface was carried out and the results are also listed in table 1. It can be seen that the HZSM-5 modified with triphenyl phosphate, TPP-CBV(8.2), gave lower conversion compared to the unmodified parent zeolite. However, the isomerization was greatly suppressed, even in the initial stage. The product distribution indicates that using larger P compound as a poison of external surface sites of HZSM-5 is an effective way to get the desirable product 4,4′-DMBP. However, it should be noted that with such a large content of P, the selectivity still remains around 55%, implying that there is still a room for enhancing the selectivity for the 4,4′-isomer.

Therefore, we further explored the effect of modification by impregnation with ammonium hydrogen phosphate (2.6 wt%). The results are shown in figures 4 and 5. From the 4-MBP conversion and the yields vs. TOS (figure 4), it can seen that even with the lower percentage of P (2.6 wt%) used here as compared to the sample of TPP-CBV(8.2), the conversion of 4-MBP over AHP-CBV(2.6) is much lower than that over TPP-CBV(8.2). This can be attributed to the different location of the phosphorus compounds on the HZSM-5 zeolite. Because of its larger size, triphenyl phosphate is mainly located on the external particle surface of HZSM-5, and the internal surface area is still relatively high even with higher P content (357 m^2/g TPP-CBV(8.2)). In the case of ammonium hydrogen phosphate, it can enter the internal surface in addition to the particle external surface, and can cause surface area decrease even at the lower P content (293 m^2/g AHP-CBV(2.6)). Moreover, over AHP-CBV(2.6) the isomerization of 4-MBP is further suppressed, and the selectivity of 4,4′-DMBP is further improved and can reach as high as 65%. Thus, our work reveals that the selectivity to the target molecule can be enhanced dramatically by simultaneous modification of the internal and external surface of HZSM-5.

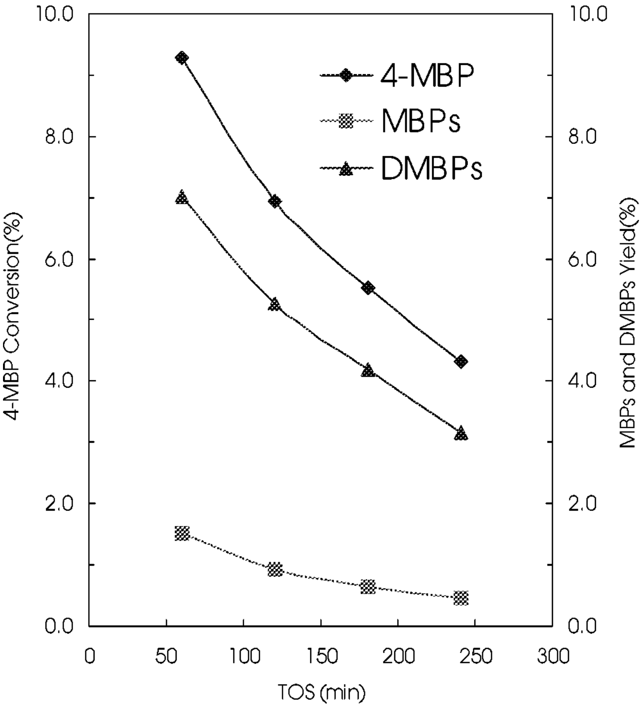

Figure 4. Conversion and yields of DMBP and MBP isomers from 4-MBP methylation over AHP-CBV.

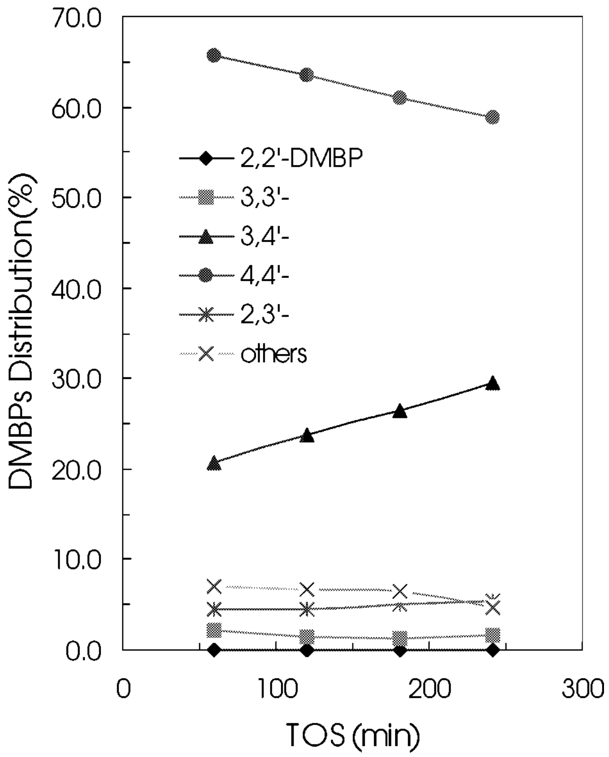

Figure 5. Distribution of DMBP isomers from 4-MBP methylation over AHP-CBV.

4. Conclusion

Methylation of 4-methylbiphenyl over different kinds of zeolites has been studied using a down-flow reactor. The 12-membered ring zeolites, HY and HM, do not show any shape selectivity, but HZSM-5 shows moderate shape selectivity to the target product, 4,4′-dimethylbiphenyl for methylation of 4-methylbiphenyl with methanol under the conditions employed. Results from examining different parameters reveal the optimal reaction conditions.

Simultaneous modification of the external and internal surface of HZSM-5 with inorganic phosphate can greatly enhance the selectivity of 4,4′-dimethylbiphenyl in the methylation reaction to as high as 65%.

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