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Shape-selective methylation of 4-methylbiphenyl to 4,4′-dimethylbiphenyl over zeolite HZSM-5 modified with metal oxides of MgO, CaO, SrO, BaO, and ZnO

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A series of ZSM-5 samples modified with metal oxides MO (M = Mg, Ca, Sr, Ba and Zn) were employed for the alkylation of 4-methylbiphenyl (4-MBP) with methanol to 4,4′-dimethylbiphenyl (4,4′-DMBP) under fixed-bed down-flow conditions. The methylation results showed that the use of basic metal oxides can effectively enhance the selectivity to the target product 4,4′-DMBP. MgO is the most effective modifier among the metal oxides used and it can improve selectivity to 4,4′-DMBP up to 80% as compared to only 13% over the parent zeolite HZSM-5. The modification effectiveness of metal oxides on 4,4′-DMBP selectivity can be arranged in the order MgO > SrO ~ ZnO ~ CaO > BaO. The optimization of MgO modification through the content, salt types and loading methods revealed that proper MgO loading (5.6 wt%) can be more effective, and the impregnation method is much better than ion exchange. The correlation of physicochemical properties (TPD, TGA, chemical analysis and chemical adsorption, etc.) of the modified HZSM-5 with the catalytic data showed that the high selectivity over ZSM-5 modified with MgO largely results from the effective suppression of 4,4′-DMBP secondary reactions such as isomerization, dealkylation and alkylation.

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

1. Introduction

Shape-selective alkylation of polycyclic hydrocarbons to symmetric intermediates such as 4,4′-dialkylbiphenyl (4,4′-DABP) and 2,6′-dialkylnaphthalene (2,6′-DAN) has been of interest for many years [1–9] because of their importance as the precursors in advanced polymer materials [10–13]. As for the preparation of 4,4′-DABP, the alkylation agents can be used with either a large group like isopropyl or small ones such as ethyl and methyl. The results in the literature show that it is extremely difficult to obtain 4,4′-dimethylbiphenyl (4,4′-DMBP) selectively through methylation [8,9]. Recently, some breakthrough on the methylation of 4-methylbiphenyl (4-MBP) with methanol was reported by Shen *et al.*, in which the selectivity to 4,4′-DMBP can be as high as 65% over HZSM-5 modified with inorganic P compound [14,15]. With these encouraging findings, in this paper we further investigated the methylation of 4-MBP with methanol over HZSM-5 modified with different metal oxides (MgO, CaO, SrO, BaO and ZnO) and correlated the modification with catalytic reaction.

2. Experimental

2.1. Preparation of the samples

Zeolite NH_4ZSM-5, CBV5014 (molar ratio of SiO_2/Al_2O_3: 50.2) and HZSM-5, CBV8020 (molar ratio of SiO_2/Al_2O_3: 77.3) were obtained from Zeolyst Int and PQ Corporation, respectively. The ammonium form was converted into the H-form by heat treatment at 540 °C for 5 h before further modification.

The samples of HZSM-5 (CBV5014) modified 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 an oven (120 °C), dried overnight and then calcined at 450 °C for 5 h. There are two steps for the preparation of ion-exchanged ZSM-5 with magnesium nitrate. First, ZSM-5 was exchanged with magnesium nitrate solution (0.1 mol/l) with a liquid-to-solid ratio of 20 at 75 °C for 2 h. This routine was repeated again to increase the exchange extent. The slurry was then filtered, washed with deionized water and dried at 120 °C. The obtained sample was calcined at 450 °C for 5 h. The ion-exchange

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routine was repeated as above except for using 0.4 mol/l magnesium nitrate solution. The chemical analysis revealed the MgO content to be 1.4 wt % on the basis of HZSM-5.

2.2. *Characterization of the samples*

The sample acidic property was measured by temperature-programmed desorption (TPD) of *n*-butylamine (*n*-BA) using an Autosorb 2910 apparatus. A certain amount of the sample (typically 0.15 g) was put into sample tube and degassed, and saturated with *n*-BA vapor at 150 °C. The adsorption of *n*-BA was recorded using a TCD from 150 to 550 °C. BET sorption of N_2 was measured using an Autosorb-1 apparatus. The samples were outgassed at 250 °C prior to measuring catalyst surface areas and total pore volumes. Micropore and mesopore volumes were calculated using the *t*-plot method.

Thermal gravimetric analysis (TGA) was done using a Mettler TG-50 thermo-balance. Approximately 15 mg of the sample was loaded in an alumina crucible and heated to 800 °C with a ramp of 10 °C/min under 100 ml/min dry air flow. The used catalyst sample was dried at 100 °C overnight before TGA.

2.3. *Catalytic test*

Methylation of 4-MBP was carried out in a fixed-bed, quartz flow reactor. About 0.30 g catalyst was placed in the middle of the tube reactor between quartz beads and activated at 450 °C for 1 h, then cooled to 300 °C. Typical reaction conditions were as follows: feed (4-MBP : methanol : mesitylene = 1 : 5 : 5 (mol ratio), the ratio used here is to obtain a miscible solution), 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 column of BETA DEX 120 (60 m × 0.25 mm). During the test, the He flow rate inside the capillary column and temperature for both detector and injector were kept at 1.5 ml/min and 300 °C, respectively, the GC oven temperature was initially kept at 145 °C, then ramped at 1 °C/min to 190 °C, and held at the final temperature for 15 min. Conversion of 4-MBP was calculated on the basis of reacted 4-MBP, selectivity to 4,4′-DMBP was calculated as the ratio of 4,4′-DMBP to all DMBP isomers.

3. Results and discussion

3.1. *Methylation of 4-MBP with methanol over modified zeolites*

Table 1 lists the results of 4-MBP methylation with methanol over HZSM-5 zeolites modified with different metal oxides. It can be seen from table 1 that over the parent zeolite HZSM-5, the selectivity to 4,4′-DMBP is less than 20%. With increasing time on stream (TOS), the catalytic activity decreases and the selectivity to 4,4′-DMBP reaches a maximum ($\sim$42%) because of coke formation, covering active sites over the zeolite surface and narrowing the pore size. Modification with metal oxides can effectively enhance the selectivity. Modification of HZSM-5 with MgO (7.5) is the most effective and can improve the selectivity to 4,4′-DMBP to as high as 80%. The selectivity to 4,4′-DMBP over modified ZSM-5 zeolites shows the following order: $\mathrm{MgO} > \mathrm{SrO} \sim \mathrm{ZnO} \sim \mathrm{CaO} > \mathrm{BaO}$. From the data in table 1, it can also be seen that modification with metal

Table 1
Methylation of 4-MBP with methanol over HZSM-5 zeolite modified with different metal oxides

Sample	TOS (min)	Conv. (%)	Yield (%)			MBP composition (%)			DMBP composition (%)					
			BP	MBPs	DMBPs	2-	3-	4-	2,2′-	3,3′-	3,4′-	4,4′-	2,3′-	Others
HZSM-5	75	64.92	1.33	48.01	13.71	1.43	56.35	42.22	0.00	21.23	52.37	13.27	10.21	2.92
	135	57.41	1.10	35.87	18.65	0.50	45.22	54.28	0.00	13.30	55.12	17.43	11.21	2.95
	290	19.73	0.69	3.41	15.53	0.00	4.08	95.92	0.00	1.48	43.98	42.63	11.40	0.52
Mg-CBV(2.8)	75	16.54	0.74	5.14	10.28	0.27	5.53	94.20	1.56	3.21	21.79	66.25	6.23	0.97
Mg-CBV(5.6)	45	8.46	0.87	3.05	4.53	0.14	3.09	96.78	5.52	0.00	13.25	77.48	3.75	0.00
Mg-CBV(7.5)	45	3.16	0.77	0.68	1.70	0.11	0.58	99.30	0.00	0.00	20.00	80.00	0.00	0.00
Ca-CBV(1.4)	75	19.79	0.59	5.18	13.22	0.11	5.96	93.93	0.91	3.33	30.56	56.35	8.25	0.61
	135	10.64	0.52	1.82	7.92	0.03	1.96	98.00	0.00	1.77	32.32	56.94	8.08	0.88
Sr-CBV(5.6)	75	17.01	0.72	3.73	11.86	0.00	4.30	95.70	0.42	2.70	30.35	57.59	8.26	0.67
	135	9.01	0.72	1.50	6.45	0.00	1.62	98.38	0.00	1.71	32.71	56.59	8.99	0.00
Ba-CBV(5.6)	75	36.35	0.68	19.87	14.47	0.24	23.55	76.21	2.28	9.05	42.23	36.70	7.67	2.07
	135	22.65	0.49	6.58	14.40	0.18	7.65	92.17	0.76	3.54	36.81	49.93	8.06	0.90
Zn-CBV(5.6)	75	17.41	0.74	5.97	9.93	0.10	6.64	93.26	1.51	2.82	31.72	54.98	8.16	0.81
	135	8.89	0.70	1.37	6.39	0.00	1.48	98.52	0.00	1.25	35.52	53.21	9.08	0.94
Zn-CBV(11.2)	75	5.29	0.70	1.11	3.32	0.06	1.10	98.84	0.00	1.51	31.63	59.34	7.53	0.00
	135	3.40	0.73	0.44	2.23	0.00	0.45	99.55	0.00	0.00	38.12	53.81	8.07	0.00

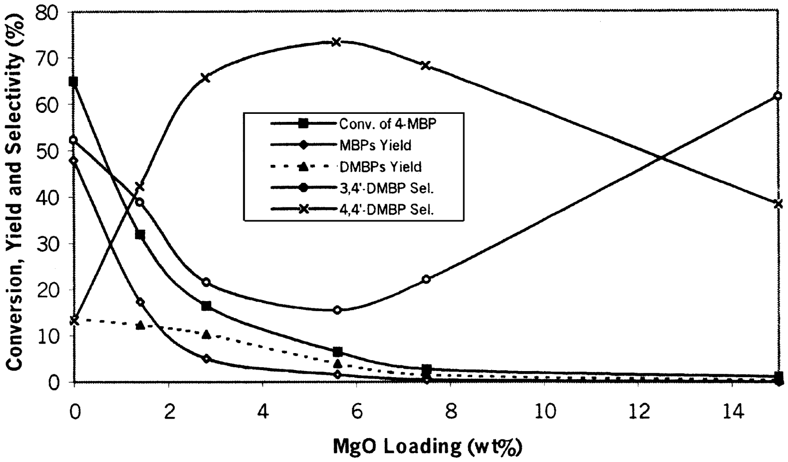

Figure 1. Effect of MgO loading on the activity and the selectivity in the methylation of 4-MBP.

oxide suppresses side reactions such as isomerization (the isomerization of 4-MBP to 3-MBP and the isomerization of 4,4′-DMBP to 3,3′-DMBP and 3,4′-DMBP). The excellent performance over Mg-CBV(x) led us to investigate further the effects of preparation methods on the selectivity to 4,4′-DMBP.

3.2. *Effect of Mg modification*

3.2.1. *MgO loading*

A wide range of MgO loading (0–14 wt%) onto zeolite was prepared by the impregnation method, as mentioned in section 2. The effects of different MgO loadings on the conversion of 4-MBP and the selectivity to 4,4′-DMBP (the data are based on the 75 min reaction results) are shown in figure 1. The selectivity to 4,4′-DMBP firstly increases, reaches a maximum (~73 wt%), and then decreases as a function of MgO content. The conversion of 4-MBP, however, decreases sharply from initially more than 60% to near 0% with an increase in MgO loading up to only 7 wt%; the product yield, similarly, follows the same trends. The dominant products at early reaction stage are the isomers of 2- and 3-MBP over the parent zeolite HZSM-5. Modification with MgO, however, can very effectively suppress the formation of these isomers, particularly at higher content of MgO (>2.0 wt%). The suppression of the isomerization of 4-MBP to 2- and 3-MBP leads to the decrease, not surprisingly, in the conversion of 4-MBP; while the suppression of the isomerization of the objective products to 3,4′-DMBP and other DMBP isomers leads to the increase in the selectivity to 4,4′-DMBP.

The XRD spectra of Mg-CBV(x) samples show that the modification with MgO still retains the ZSM-5 structure; nevertheless, the relative crystallinity decreases with increasing of the loading of MgO. No crystalline MgO was detected in the XRD spectra until the MgO loading is more than 15%. The XRD-undetectable MgO phase may have been highly dispersed onto the surface of ZSM-5, as evidenced by Xie *et al.* [16]. The surface area of MgO-modified ZSM-5 zeolites is listed in table 2. It can be seen from table 2 that both the surface area and micro-porosity decrease, not surprisingly, with an increasing 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 large molecular *n*-BA also supported the BET results by observing the lower acidity over the samples with a larger amount of magnesium oxide.

The coke content over spent catalysts was analyzed using TGA and the results are summarized in table 3.

Table 2
Properties of MgO-modified HZSM-5 samples[a]

Sample	Surface area, m^2/g			Porosity, cm^3/g		
	Total	Micro	Meso	Total	Micro	Meso
Mg-CBV(0)	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

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

Table 3
Weight loss of the Mg-CBV(x) and Zn-CBV(x) samples

Sample	Weight loss (%) (350–650 °C)	Decomposition temperature (°C)
HCBV5014	10.83	545.0
Mg-CBV(1.4)	7.20	498.3
Mg-CBV(2.8)	5.64	498.3
Mg-CBV(5.6)	5.86	465.0
Mg-CBV(7.5)	4.10	491.7
Zn-CBV(1.4)	10.98	521.7
Zn-CBV(2.8)	9.60	488.3
Zn-CBV(5.6)	8.38	471.7

Table 4
Methylation of 4-MBP with methanol over HZSM-5 zeolite modified with different methods

Sample	TOS (min)	Conv. (%)	Yield (%)			MBP composition (%)			DMBP composition (%)					
			BP	MBPs	DMBPs	2-	3-	4-	2,2′-	3,3′-	3,4′-	4,4′-	2,3′-	Others
Mg-CBV(1.4)	75	31.95	0.82	17.44	12.31	0.30	20.10	79.60	1.62	7.88	38.91	42.40	8.61	0.57
	135	25.88	0.72	10.03	13.76	0.14	11.78	88.08	1.24	4.58	34.38	49.93	9.16	0.73
Mg-CBVIE(0.2)	75	56.44	1.25	39.46	12.81	0.86	46.68	52.47	0.00	17.02	51.76	17.80	9.91	3.51
	135	50.25	0.94	28.24	17.96	0.31	35.90	63.79	0.00	10.75	52.78	23.16	10.91	2.39
Mg-CBVIE(1.4)	75	22.33	0.66	11.10	10.45	0.17	12.34	87.50	2.20	5.93	27.94	56.17	6.99	0.77
	135	17.20	0.55	5.27	10.89	0.17	5.81	94.02	2.11	3.67	24.06	62.44	6.70	1.01

It can be seen from table 3 that, as compared with the parent zeolite, modification of zeolite with basic oxide obviously reduces the formation of coke during methylation of 4-MBP (10.83% over the parent HZSM-5 vs. 4.10% over Mg-CBV(7.5)). The results also demonstrated that with the increasing MgO (from 1.4 to 7.5 wt%) and ZnO content (from 1.4 to 5.6 wt%), the decreasing of acid sites resulting from the neutralization with basic oxides is responsible for the reduced coke formation. At the same time, the narrowed pore channel, as evidenced by the lower micro-porosity (table 2), also restricts the large-molecule coke formation and, therefore, favors the selectivity to the smallest and most linear molecule 4,4′-DMBP among its isomers.

3.2.2. *Preparation method*

Two metal loading methods through ion exchange (Mg-CBVIE) and impregnation (Mg-CBV) were employed for MgO-modified catalysts and their catalytic properties are listed in table 4. It can be seen that MgO-modified catalyst from ion exchange (CBVIE) exhibits higher selectivity to 4,4′-DMBP at a similar MgO loading of 1.4 wt%: 49.93% over Mg-CBV(1.4) vs. 62.44% over Mg-CBVIE(1.4). The possible reason is that over the ion-exchanged sample, MgO is highly dispersed. Usually, more metal loading is necessary to achieve higher product selectivity. However, from the viewpoint of catalyst preparation, it is much more difficult to get high MgO loading through the ion-exchange method. For example, MgO loading is only 0.2% after initial ion exchange, and after repeating the ion exchange three times, MgO loading is only up to 1.4%.

3.2.3. *Mg modifier*

The effects of anions of Mg salts on 4-MBP methylation were investigated using CBV8020 and the results are shown in figure 2. It can be seen that Mg^{2+}-modified zeolite catalysts exhibit similarity in the conversion of 4-MBP but slight differences in the selectivity to 4,4′-DMBP, which can be arranged in the following order: $NO_3^- > CH_3COO^- \sim Br^- > Cl^-$. The lower selectivity with Cl^- could result from the Cl^- residing in the catalyst after calcination, leading to the increase in the acid properties, and so resulting in the lower selectivity to 4,4′-DMBP.

3.3. *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- and ZnO-modified

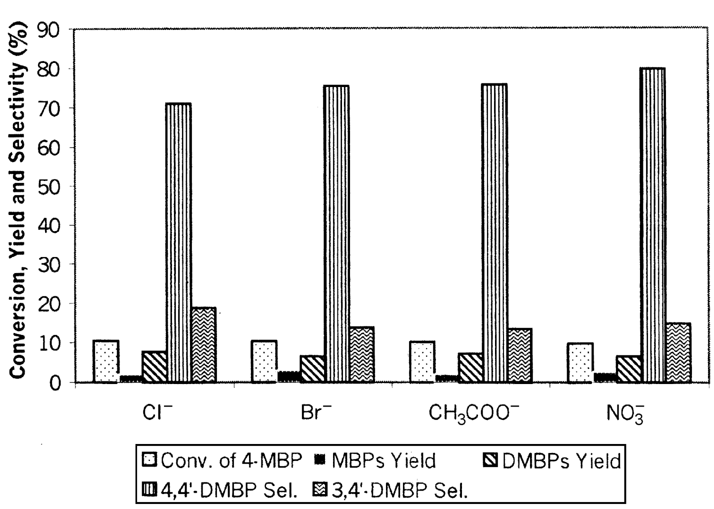

Figure 2. Effect of anion on the conversion of 4-MBP and the selectivity to 4,4′-DMBP.

Table 5
Reaction of 4,4′-DMBP[a] over HCBV5014, Mg-CBV(5.6) and Zn-CBV(5.6) catalysts under methylation conditions[b]

Sample	HZSM-5	Mg-CBV(5.6)	Zn-CBV(5.6)
4,4′-DMBP conversion (%)	87.95	9.8	41.17
Product distribution (%, change)			
BP	0.18 (0.18)	0 (0)	0 (0)
2,2′-DMBP	0.12 (0.12)	0 (0)	0 (0)
2-MBP	0.14 (0.14)	0.12 (0.12)	0.05 (0.05)
3-MBP	3.17 (3.17)	0 (0)	0.51 (0.51)
4-MBP	10.81 (10.71)	1.54 (1.44)	2.11 (2.01)
3,3′-DMBP	20.91 (20.83)	1.38 (1.30)	4.63 (4.55)
3,4′-DMBP	45.37 (45.16)	6.54 (6.33)	30.083 (30.62)
4,4′-DMBP	12.00 (−87.61)	89.85 (−9.76)	58.60 (−41.01)
2,3′-DMBP	0.60 (0.60)	0 (0)	0.18 (0.18)
Other DMBP	3.18 (3.18)	0 (0)	0.12 (0.12)
Tri- and polymethylbiphenyl	3.51 (3.51)	0.56 (0.56)	2.98 (2.98)

[a] The composition of raw material 4,4′-DMBP: 4-MBP, 0.10%; 3,3′-DMBP, 0.08%; 3,4′-DMBP, 0.21%; 4,4′-DMBP, 99.61%.

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

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 investigated under the same reaction condition as the methylation of 4-MBP. The reaction results are listed in table 5, together with the results over the parent zeolite. As can be seen from table 5 the conversion of 4,4′-DMBP is about 88% over HCBV5014 and the main products are DMBP (about 70%, from isomerization), MBP (14%, from dealkylation) and tri- and polymethylbiphenyl (3–4%, from alkylation). Over the 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 polymethylbiphenyl (about 0.5%, from alkylation). The comparison reveals that the yields of DMBP, MBP and polymethylbiphenyl greatly decrease after modification. A 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 ZSM-5 zeolites.

4. Conclusion

A series of HZSM-5 zeolites modified with MgO, CaO, SrO, BaO and ZnO was prepared through the impregnation method and employed for methylation of 4-MBP with methanol to 4,4′-dimethylbiphenyl. The results show that the modification with metal oxide can effectively improve the selectivity to 4,4′-DMBP. ZSM-5 modified with MgO can increase the selectivity to 4,4′-DMBP up to 80%, and about 60% by modification with ZnO, CaO and SrO. The increase of selectivity to the target molecule mainly comes about from the decrease of acid sites and the narrowed pore channel of ZSM-5. As a result, side reactions such as isomerization, polyalkylation and dealkylation of 4,4′-DMBP are suppressed.

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