Tert-butylation of biphenyl over mordenites

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H-mordenites are very highly shape-selective catalysts in the alkylation of biphenyl with *tert*-butanol under liquid phase conditions using *n*-decane as a solvent with a selectivity to 4-(*tert*-butyl)biphenyl above 98% and to 4,4′-di(*tert*-butyl)biphenyl near 100% to give 24% yield of 4,4′-di(*tert*-butyl)biphenyl using H-MOR(45).

KEY WORDS: alkylation; biphenyl; *tert*-butanol; H-mordenites

1. Introduction

H-mordenites have been found to be the most suitable catalysts for selective isopropylation of polynuclear aromatic hydrocarbons such as biphenyl [1,2] and naphthalene [3,4] with propylene. Especially highly dealuminated H-mordenites have shown high selectivity for 4,4′-di(isopropyl)biphenyl [5,6]. A 98% conversion of biphenyl and 72% yield of 4,4′-di(isopropyl)biphenyl have been obtained over highly dealuminated mordenite with SiO_2/Al_2O_3 molar ratio 2600 by Lee and co-workers [7]. In order to suppress the side reactions and isomerization of products at the outer surface of mordenites, Sugi and coworkers [8] have used mordenites modified by impregnation with ceria.

Recently, we reported that H-Y and H-Beta zeolites were effective catalysts for the shape-selective alkylation of biphenyl with *tert*-butanol under mild reaction conditions [9]. Selectivities to 4-(*tert*-butyl)biphenyl (4-MTBB) above 90% and to 4,4′-di(*tert*-butyl)biphenyl (4,4′-DTBB) up to 80% were achieved over both types of zeolites. However, besides the desired 4-MTBB and 4,4′-DTBB, secondary products, identified as higher mono- and dialkylbiphenyls, were produced in certain amounts. These compounds could be formed by alkylation of biphenyl with lower oligomers of isobutylene, generated by dehydration of *tert*-butanol.

Moreover, an unusual transalkylation of MTBB derivatives with cyclohexane used as a solvent has been observed over H-Beta zeolite leading to the formation of cyclohexyl- and methylcyclopentylbiphenyls [10].

The present paper deals with the use of H-mordenites with varied Si/Al ratios as catalysts in the *tert*-butylation reaction of biphenyl with *tert*-butanol as alkylating agent in *n*-decane as solvent. The main objective of this work was to achieve a high 4,4′-DTBB selectivity by suppressing the possible side reactions observed over large-pore H-Y and H-Beta zeolites.

2. Experimental

2.1. Catalysts and chemicals

All zeolites (CBV 20A, CBV 30A, CBV 90A, CBV 720, CP 814E) used as precursors of catalysts were from PQ Corporation. The surface areas of the zeolites were determined by adsorption of nitrogen at the temperature of liquid nitrogen using a Sorptomatic 1 900 instrument. Total acidity was measured by temperature-programmed desorption using ammonia as probe molecule. The apparatus and procedure are described elsewhere [11]. The characteristics of the studied zeolites are listed in table 1.

Calcination of zeolites was performed in a flow of dry air at 500 °C for 6 h with a heating rate of 60 $°C\,h^{-1}$ from room temperature to 500 °C.

2.2. Catalytic runs

The alkylation reactions were carried out in a 0.150 l stirred reactor with agitation speed 2000 min^{-1}. In a typ-

Table 1
Properties of zeolites.

Catalyst		SiO_2/Al_2O_3 (mol. ratio)	S_{BET} ($m^2\,g^{-1}$)	a_{total} (mmol-H^+ g^{-1})
H-Y(15)	CBV 720	30	697	0.56
H-Beta(12.5)	CP 814E	25	681	1.03
H-MOR(10)	CBV 20A	20	403	1.3
H-MOR(17.5)	CBV 30A	35	497	0.92
H-MOR(45)	CBV 90A	90	468	0.38

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ical run, biphenyl (1.54 g, 10 mmol), *tert*-butanol (1.48 g, 20 mmol) and 100 ml *n*-decane (cyclohexane) as a solvent were mixed in the reactor and freshly calcined zeolite (0.5 g) kept at 200 °C was then added. The reactor was closed and flushed with nitrogen. The standard reaction temperature was 160 °C and pressure (3.5 MPa) was controlled with nitrogen.

2.3. Analytical method

Samples of reaction mixture were withdrawn periodically from the closed reactor and analyzed on a Chrompack 9002 gas chromatograph equipped with a CP-Sil 5 CB capillary column (10 m × 0.32 mm) and FID detector. The temperature program was: 60 °C (5 min), from 60 to 275 °C with a ramp of 5 °C min^{-1} and at 275 °C 5 min isothermally.

The main and secondary products were identified by GC-MS analysis. Conversion of biphenyl (X_{BP}) was calculated on the basis of reacted biphenyl. Selectivity to 4-(*tert*-butyl)biphenyl (4-MTBB) and to 4,4′-di(*tert*-butyl)biphenyl (4,4′-DTBB) was calculated as the ratio of 4-MTBB to all MTBB isomers and of 4,4′-DTBB to all DTBB isomers, respectively.

3. Results and discussion

The alkylation of biphenyl with *tert*-butanol was carried out over H-MOR under the same reaction conditions as those used over H-Y and H-Beta using cyclohexane as solvent [9]. The results obtained for the different types of zeolites are listed in table 2.

The final biphenyl conversion (56% after 8 h reaction) obtained over H-MOR(17.5) is very close to that for H-Y(15) (58%). Concerning the product distribution, a similar selectivity for the monoalkylation step is observed, MTBB are formed preferentially (66% of MTBB for H-MOR(17.5), 62% for H-Y(15) and 75% for H-Beta(12.5), respectively, after 2 h reaction).

Nevertheless, H-mordenite appears to be more selective towards the formation of the *para* derivative 4-MTBB (>99%) and of the *para*, *para′* dialkylated analog 4,4′-DTBB (up to 93% after 8 h reaction against 77 and 60%, respectively, for H-Y(15) and H-Beta(12.5)). Moreover, the amount of by-products, so-called the other alkylbiphenyls (OAB), over H-MOR(17.5) zeolite is lower in comparison with the two other H-Y and H-Beta zeolites (11% OAB for H-MOR(17.5), 19% for H-Y(15), 21% for H-Beta(12.5), respectively, after 8 h reaction).

Thus, reaction results clearly show that pore architecture and pore dimensions of H-mordenites having twelve-membered ring elliptical pores (0.67 × 0.71 nm) and eight-membered ring pores (0.29 × 0.57 nm) [12] are suitable for the shape-selective *tert*-butylation of biphenyl under mild reaction conditions.

The formation of secondary products, generated by reaction of MTBB with cyclohexane used as solvent in the alkylation of biphenyl with *tert*-butanol, was observed under certain reaction conditions especially over H-Beta zeolite at higher temperatures [10]; the occurrence of such a reaction has been avoided by using *n*-decane as the solvent. The *tert*-butylation of biphenyl over H-mordenite has been thus carried out under the standard conditions using *n*-decane as sol-

Table 2
Reaction results of biphenyl *tert*-butylation in cyclohexane over zeolite catalysts at 160 °C.[a]

Zeolite catalyst	Time (min)	X_{BP} (%)	Distribution of products (%) 4-MTBB	$\sum$MTBB	4,4′-DTBB	$\sum$DTBB	$\sum$OAB	$S_{4\text{-MTBB}}$ (%)	$S_{4,4'\text{-DTBB}}$ (%)
H-Y(15)	120	55.6	59.7	62.4	16.9	20.8	16.7	95.7	81.2
	480	58.1	58.7	62.5	14.4	18.6	18.9	93.9	77.4
H-Beta(12.5)	120	40.2	63.2	74.6	12.9	16.2	9.2	84.7	79.6
	480	37.2	33.1	52.9	15.6	26.1	20.9	62.6	59.8
H-MOR(17.5)	120	37.3	65.9	66.2	26.8	27.9	5.9	99.5	96.1
	480	56.1	64.2	64.7	22.6	24.2	11.1	99.2	93.4

[a] Reaction conditions: biphenyl 10 mmol, *tert*-butanol 20 mmol, catalyst 0.5 g, cyclohexane 100 ml, $p = 2.0$ MPa.

Table 3
Reaction results of biphenyl *tert*-butylation in *n*-decane over zeolite catalysts at 160 °C.[a]

Zeolite catalyst	Time (min)	X_{BP} (%)	Distribution of products (%) 4-MTBB	$\sum$MTBB	4,4′-DTBB	$\sum$DTBB	$\sum$OAB	$S_{4\text{-MTBB}}$ (%)	$S_{4,4'\text{-DTBB}}$ (%)
H-Y(15)	120	34.0	57.3	67.6	15.9	21.2	11.2	84.8	75.0
	480	51.9	55.3	64.2	15.8	20.6	15.2	86.1	76.6
H-Beta(12.5)	120	34.2	49.1	66.7	15.5	20.2	13.1	73.7	76.7
	480	54.0	38.8	61.3	6.3	13.5	25.2	63.3	46.6
H-MOR(17.5)	120	46.5	48.0	48.6	42.4	42.6	8.8	98.8	99.5
	480	66.9	56.1	56.8	20.2	20.9	22.3	98.8	96.6

[a] Reaction conditions: biphenyl 10 mmol, *tert*-butanol 20 mmol, catalyst 0.5 g, *n*-decane 100 ml, $p = 3.5$ MPa.

vent and compared with H-Y and H-Beta. Table 3 shows the results thus obtained.

It can be seen first, that a maximum biphenyl conversion of 67% has been achieved over H-MOR(17.5), while this maximum was only up to 54% for H-Y and H-Beta. On the other hand, the comparison of tables 2 and 3 shows that, in the case of H-Y and H-Beta zeolites, *n*-decane as a solvent does not prove to be more suitable than cyclohexane from the point of the distribution of reaction products or selectivities to 4-MTBB and 4,4′-DTBB (selectivity to 4-MTBB near 94% and selectivity to 4,4′-DTBB 77% for H-Y(15) in cyclohexane against selectivity to 4-MTBB 86% and to 4,4′-DTBB 77% for H-Y(15) in *n*-decane after 8 h reaction). Even by using *n*-decane as the solvent, the monoalkylation step remained more significant in comparison with dialkylation over both H-Y(15) and H-Beta(12.5) zeolites (68% of MTBB to 21% of DTBB for H-Y(15), 67% of MTBB to 20% of DTBB for H-Beta(12.5) after 2 h).

In the case of H-MOR(17.5), a beneficial influence of *n*-decane is found not only from the point of the selectivities to 4-MTBB (about 99%) and 4,4′-DTBB (up to 97%), but especially from the point of the distribution of reaction products. As shown in figure 1, such a distribution of reaction products for H-MOR(17.5) in *n*-decane is quite different from that in cyclohexane under the same reaction conditions.

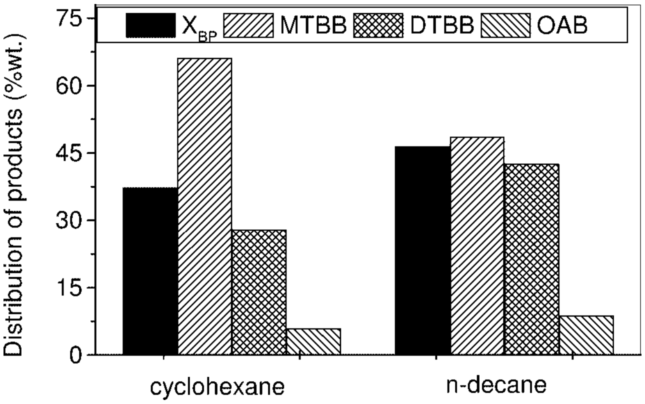

Figure 1. Distribution of reaction products for H-MOR(17.5) in different solvents. Reaction conditions: H-MOR(17.5) 0.5 g, BP 10 mmol, *t*-BuOH 20 mmol, $T = 160\,^{\circ}\mathrm{C}$, solvent 100 ml, $p = 3.5$ MPa, 2 h.

The use of *n*-decane leads to a significant increase of the amount of the di(*tert*-butyl)biphenyls in the reaction mixture (43% of DTBB in *n*-decane with a 99.5% selectivity to 4,4′-DTBB after 2 h reaction against 28% of DTBB in cyclohexane). Thus, H-mordenite with Si/Al = 17.5 has been shown to be a more selective catalyst for di *tert*-butylation of biphenyl than H-Y and H-Beta with corresponding Si/Al ratios.

Further studies have been aimed at using H-MOR zeolite catalysts and *n*-decane as a solvent at the temperature 160 °C with the aim to enhance the conversion of biphenyl into di(*tert*-butyl)biphenyls while retaining the high selectivity.

Reaction results of biphenyl *tert*-butylation with *tert*-butanol over H-mordenites with varied silicon/aluminium molar ratio under improved reaction conditions are listed in table 4.

All H-mordenites show high catalytic activity for the studied reaction with a biphenyl conversion about 70% at 8 h reaction (table 4). Such a conversion does not increase significantly after longer time of reaction. This is mainly due to a certain deactivation of the active sites of the catalyst with reaction time by the oligomerization of excess olefin produced by *tert*-butanol dehydration, as it has been shown in previous works in biphenyl [9] and naphthalene [13] series.

However, changing the Si/Al ratio of H-mordenites has not any significant influence on the selectivity to 4-MTBB and 4,4′-DTBB at a similar conversion of biphenyl (selectivity to 4-MTBB about 99% and to 4,4′-DTBB near 100% was achieved over all H-MOR samples). Such a selectivity to 4,4′-DTBB slightly decreases during the last 2 h reaction, which is certainly due to the isomerization of 4,4′-DTBB to 3,4′-DTBB while selectivity to 4-MTBB remains nearly constant *versus* reaction time.

Table 4

Reaction results of biphenyl *tert*-butylation in *n*-decane over H-mordenite catalysts at 160 °C.[a]

Mordenite	Time	X_{BP}	Distribution of products (%)					$S_{4\text{-MTBB}}$	$S_{4,4'\text{-DTBB}}$
catalyst	(min)	(%)	4-MTBB	$\sum$MTBB	4,4′-DTBB	$\sum$DTBB	$\sum$OAB	(%)	(%)
H-MOR(10)	30	28.3	49.1	50.5	43.5	43.5	6.0	97.2	100
	60	42.1	47.0	48.0	43.7	43.7	8.3	98.0	100
	120	55.4	47.1	48.0	42.2	42.6	9.4	98.1	99.1
	480	67.9	52.3	53.6	15.3	17.2	29.2	97.5	98.9
H-MOR(17.5)	30	26.6	47.7	48.5	44.4	44.4	7.1	98.4	100
	60	38.5	47.8	48.6	43.6	43.6	7.8	98.4	100
	120	46.5	48.0	48.6	42.4	42.6	8.8	98.8	99.5
	480	66.9	56.1	56.8	20.2	20.9	22.3	98.8	96.6
H-MOR(45)	30	21.7	50.2	50.2	47.9	47.9	1.8	100	100
	60	35.6	42.4	42.7	53.9	54.2	3.1	99.3	99.5
	120	44.3	43.1	43.1	52.4	52.6	4.3	100	99.6
	480	70.0	52.8	53.0	31.1	31.4	15.6	99.7	99.0

[a] Reaction conditions: biphenyl 10 mmol, *tert*-butanol 20 mmol, catalyst 0.5 g, *n*-decane 100 ml, $p = 3.5$ MPa.

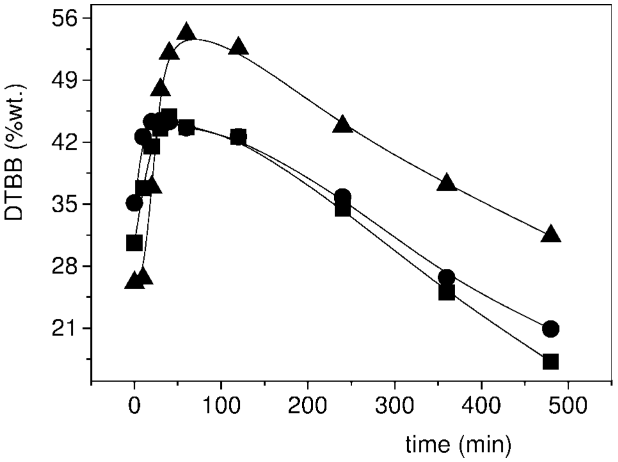

Figure 2. Dependence of DTBB distribution *versus* reaction time. Reaction conditions: catalyst 0.5 g, *t*-BuOH 20 mmol, BP 10 mmol, $T = 160\,^{\circ}$C, $p = 3.5$ MPa. (■) H-MOR(10), (•) H-MOR(17.5) and (▲) H-MOR(45).

Concerning the distribution of reaction products, the monoalkylation step is comparable with dialkylation (about 48% of MTBB and 44% of DTBB after 1 h reaction over H-MOR(10) and H-MOR(17.5), respectively). In the case of H-MOR(45), mono *tert*-butylated derivatives are produced in less extent than di *tert*-butylated (43% of MTBB, 54% of DTBB after 1 h reaction).

A maximum of di(*tert*-butyl)biphenyl derivatives over all studied H-mordenites is observed after 1 h reaction and then their amount decreases considerably with reaction time, as shown in figure 2.

This decrease of di(*tert*-butyl)biphenyls corresponds to an increase of mono(*tert*-butyl)biphenyls and of the other alkylbiphenyls, which can be explained by partial dealkylation of DTBB into MTBB and next alkylation of mono *tert*-butylated derivatives with longer alkenes, especially with oligomers of isobutylene to give the other *tert*-butylalkylbiphenyls, as shown in previous work [10]. The occurrence of a partial dealkylation of di(*tert*-butyl)biphenyls was supported experimentally when the most acidic H-MOR(10) (table 1), freshly calcined and *n*-decane as a solvent were added to the reaction product obtained after 1 h reaction over H-MOR(45) containing 37% of MTBB, 55% DTBB and 8% OAB. After 1 h reaction, increase of MTBB (37–48%) and OAB (8–21%) with a corresponding decrease of DTBB (55–31%) was observed.

Finally, our results show that the catalytic activity of the H-mordenites for the formation of the other alkylbiphenyls can be set in the order: H-MOR(10) > H-MOR(17.5) > H-MOR(45) (figure 3).

This result is connected most probably with the acidity of H-mordenites. H-MOR(10) was shown to be the most acidic in comparison with H-MOR(17.5) and H-MOR(45) (table 1). High density of the acidic sites of H-MOR(10) can lead to higher concentration of isobutyl carbenium ions on the surface and it would favour the monoalkylation step, but also would enhance isobutylene side reactions and, finally, coking of catalytically active sites. Over dealuminated H-MOR(45), the experimental results suggest that reducing of acidity by dealumination can make acidic sites more selective for the formation of di(*tert*-butyl)biphenyls at the expence of secondary reactions.

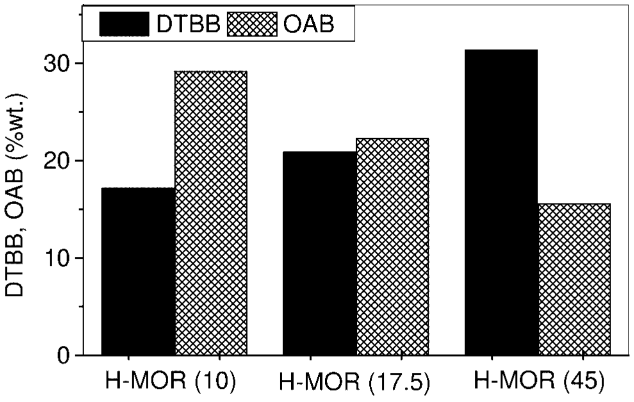

Figure 3. Distribution of DTBB and other alkylbiphenyls over H-mordenites. Reaction conditions: catalyst 0.5 g, *t*-BuOH 20 mmol, BP 10 mmol, $T = 160\,^{\circ}$C, $p = 3.5$ MPa, *n*-decane 100 ml, 8 h.

4. Conclusion

Highly shape-selective alkylation of biphenyl with *tert*-butanol was achieved over H-mordenite catalysts. In all cases, conversion of biphenyl up to 70% after 8 h reaction was obtained under standard reaction conditions using *n*-decane as a solvent at the temperature 160 °C. H-mordenites with various Si/Al ratios display very high stereoselectivity of both mono *tert*-butylation and di *tert*-butylation steps leading to selectivity for 4-MTBB about 98% and for 4,4′-DTBB near 100%. Over dealuminated H-MOR(45) the conversion of biphenyl into di(*tert*-butyl)biphenyls is enhanced while retaining the high selectivity. 54% of DTBB against 43% of MTBB is obtained after 1 h reaction over H-MOR(45) to give a total 24% yield of 4,4′-di-(*tert*-butyl)biphenyl.

Thus, dealuminated H-mordenites, which have been found to be highly selective catalysts for isopropylation of polynuclear aromatic hydrocarbons such as biphenyl and naphthalene, are shown to be the most selective for *tert*-butylation of biphenyl under liquid phase conditions.

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