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Shape-selective alkylation of biphenyl with propylene using zeolite and amorphous silica-alumina catalysts



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ABSTRACT

The influence of zeolite structure for the alkylation of biphenyl with propylene was studied over various zeolites such as HY, HZSM-5, and dealuminated mordenite (DMOR), as well as amorphous SiO₂/Al₂O₃, in a stirred tank reactor. Biphenyl conversion was found to increase with reaction time for HZSM-5 and DMOR zeolites and reach a leveling off in 4 h, whereas for HY and amorphous SiO₂/Al₂O₃ a leveling off was reached within an hour. DMOR displayed the highest selectivity for 4,4'-diisopropylbiphenyl (4,4'-DIPB) even at temperatures as high as 300 °C, whereas for HY, HZSM-5 and amorphous SiO₂/Al₂O₃ selectivities fell in the range of 10–35%; they were significantly lower than observed for DMOR. These differences in selectivity might be due to the structure and pore channels of the zeolites. DMOR was found to be an active catalyst, the selectivity for 4,4'-DIPB) isomers, respectively, indicating DMOR possesses shape-selectivity. The selectivity of 4,4'-DIPB increased with time, while the corresponding selectivity of 4-IPB decreased for DMOR catalyst. Alkylation of biphenyl with propylene occurred with predominant formation of 4-IPB in the first step. 4-IPB is only a source in the second step of alkylation of DIPB isomers.

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1. Introduction

The alkylation of biphenyl with propylene is a reaction of practical interest since it produces 4,4'-diisopropylbiphenyl (4,4'-DIPB) [1–5]. 4,4'-DIPB is a promising precursor for biphenyl-4,4'-dicarboxylic acid, which is an intermediate for polyester fibers, engineering plastics, liquid crystalline polymers for electronic and mechanical devices, and films with high heat resistance and strength [6,7]. Selective synthesis of 4,4'-DIPB is not possible on traditional Friedel-Crafts [8] catalysts such as Lewis acids or silica/alumina [9], which generally produce large amounts of undesired products having low para-selectivity. In contrast, zeolites, being microporous and crystalline, shape-selectively yield the least bulky para-isomers [10]. Zeolite catalysts are attractive for several reasons: enhanced selectivity of the desired product, easy separation, and reusability; most importantly, they are environmentally benign materials. Shape selectivity characteristics of zeolites in alkylation of biphenyl can therefore be very useful for the synthesis of linear 4,4'-dialkylbiphenyl derivatives.

Alkylation of biphenyl with propylene has been successfully demonstrated by numerous research groups using a variety of catalysts. Valuable insights into the controlling factors and their influence on the conversion and selectivity are well documented. Accordingly, existing catalysts were compared, and a few modified or new catalysts were developed and tested to further enhance desired product selectivity. A 98% conversion of biphenyl and 72% yield of 4,4'-DIPB have been obtained over highly dealuminated mordenite at 250 $^\circ\text{C}$ with SiO_2/Al_2O_3 molar ratio of 2600 by Lee et al. [11]. Out of Na-mordenite, ZSM-5, HY and dealuminated Y tested for this reaction, Vergani et al. [12] found that the mordenite catalyst had the best performance and was most selective toward 4,4'-DIPB. Matsuda et al. [13] investigated HY, H-beta, H-mordenite, H-offretite, H-ZSM-8, H-ZSM-5 and silica/alumina catalysts. They found that mordenite was the most active for the isopropylation of biphenyl with 40% conversion and 7% yield of 4,4'-DIPB at 250 °C. Exchange of 55% of Na cations of mordenite with protons was found to increase the DIPB yield. Low yields of 7% with unmodified H-mordenite were attributed to the presence of strong acid sites, especially on the external catalyst surface, which catalyze the isomerization of 4,4'-DIPB. Impregnation of mordenite with phosphoric acid blocks Al sites on the outer surface, thus effectively suppressing isomerization. Loktev and Chekriy [14] studied this reaction over zeolites Y, Beta, mordenite, ZSM-5 and ZSM-12.

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Table 1			
Physical	properties	various	zeolites.

Catalyst	SiO ₂ /Al ₂ O ₃ ratio	BET surface area (m ² /g)	Single point pore volume (cm ³ /g)	BJH _{ads} pore volume (cm ³ /g)	Acidity ratio (Lewis/Brønsted)	Ammonia adsorption ^a
НҮ	30.0	783.8	0.506	0.204	1.743	16.5
HZSM-5	20.0	364.7	0.200	0.058	0.273	4.7
HMOR	6.1	449.8	0.308	0.143		1.3
DMOR	45.7	434.2	0.315	0.148	1.192	1
SiO ₂ -Al ₂ O ₃	5.1	427.1	0.701	0.721	2.375	1.9

^a Ammonia adsorption related to dealuminated mordenite.

They related the activity and selectivity of the catalysts with their pore structures and concluded that the constraint effects present in mordenite and ZSM-12 zeolites are needed to obtain a high selectivity to 4,4'-DIPB. Matsuda et al. [15,16] poisoned external acid sites of mordenite with tributylphosphite to enhance the yield of 4,4'-DIPB, thus suppressing the side reactions of propylene. Cerium has a similar effect and deactivates the external acid sites of Hmordenite without choking its pores [17]. At 300 °C the selectivity toward 4,4'-DIPB was enhanced from 40% to 85% by cerium modification, while the conversion of biphenyl was unaltered at 95%. Recently Sugiet al. [18-22] reported shape-selective isopropylation of biphenyl over many types of zeolites. Bandyopadhyay et al. [23] reported that unmodified SAPO-5 at 300 °C converted 98% biphenyl with 35% selectivity toward DIPB. Modification of SAPO-5 with ceria blocked the external acid sites preventing non-regioselective reactions on external surfaces. This resulted in an improvement of the selectivity for 4,4'-DIPB.

Among zeolite catalysts, mordenite (MOR) type zeolite possesses particularly good shape selectivity characteristics for the alkylation of biphenyl with propylene [1,2,11,12,24,25]. In comparison with low silica MOR catalysts, highly dealuminated MOR catalysts displayed high activity and improved selectivity in the alkylation of biphenyl with propylene. The purpose of the present work is to systematically examine changes in conversion and selectivity with reaction time using different zeolites, and to achieve both high activity and high 4,4'-diisopropylbiphenyl selectivity. The present study explores the use of propylene as the alkylating agent in the alkylation of biphenyl over various zeolites such as HY, HZSM-5, and DMOR as well as amorphous silica alumina as catalysts under liquid phase conditions. From these findings, a plausible mechanism is proposed for the selective formation 4,4'-DIPB over dealuminated mordenite catalyst.

2. Experimental

H-mordenite (HMOR), having a Si/Al ratio of 6, and the NH₄ form of ZSM-5, were obtained from Clariant Inc., Louisville, and HY zeolite was purchased from Alfa Aesar. For dealumination, H-MOR was then refluxed with 6 N HNO₃ solution for 3 h, using 15 mL of solution/gram of HMOR. After the acid treatment, the samples were washed with water to remove residual nitrate, and the washing procedure was repeated twice. The resulting material was dried overnight at 383 K and calcined statically under an ambient atmosphere at 823 K for 12 h, and it is denoted as DMOR (dealuminated mordenite). The NH₄ form of ZSM-5 was converted to the hydrogen form by calcining the catalyst from room temperature to 823 K (held for 12 h), at a ramp rate of 5 K/min under air flow.

The surface areas, pore volumes, and average pore radii of the catalysts were measured by BET using a Micromeritics Tri-Star 3000 gas adsorption analyzer system. Nitrogen was used as the adsorption gas and sample analysis was performed at 77 K. Prior to the measurement, the samples were slowly ramped to 433 K and evacuated overnight to approximately 50 mTorr. Pore

size distributions (PSD) of the catalysts were quantified by the Barrett, Joyner, Halenda (BJH) desorption model, which provides a relationship whereby the amount of adsorbate lost during a desorption step gives the average size of the pore emptied during that desorption step. Physical properties are presented in Table 1.

The nature of the acid sites (Brønsted or Lewis) was determined by FT-IR of chemisorbed pyridine. All spectra were recorded on a Thermo Nicolet Nexus 870 Fourier-transform infrared spectrometer. The samples (\sim 22 mg) were ground to a fine powder, which were then placed into an infrared cell and outgassed at 400 °C for 3 h as a pretreatment procedure to clean the surface and eliminate possible impurity prior to adsorption of the base. The sample was cooled to 150 °C, and pyridine was dosed until saturation adsorption was achieved. After 1 h of adsorption, the excess and weakly adsorbed pyridine was removed by evacuation at the same temperature for 1.5 h. In order to measure the acid strength, pyridine absorption was carried out at 150 °C, and the corresponding spectra were recorded.

Catalysts performance for the alkylation of biphenyl with propylene was evaluated at 300 °C using a 1L stirred tank reactor equipped with a magnetically driven stirrer with turbine impeller, a gas-inlet line, and a vapor outlet line with a stainless steel (SS) fritted filter $(2 \mu m)$ placed external to the reactor (Fig. 1). In a typical run, 2.1 moles of biphenyl and 3.5 g of catalyst were introduced into the reactor. Prior to heating, the reactor was purged with nitrogen and heated to attain the desired reaction temperature. After reaching the reaction temperature, propylene gas was introduced to the reactor and the pressure kept constant (1.0 MPa) during the reaction. The propylene gas entered the reactor below the stirrer, which was operated at 500 rpm. The reactor temperature was maintained constant $(\pm 1 \,^{\circ}C)$ using a temperature controller. After flowing the propylene gas, reaction products were periodically sampled and analyzed off-line, using a HP 5890 gas chromatograph with a flame ionization detector and a 50 m DB-5 column. Reaction products were also confirmed with an Agilent 5975N Mass Selective Detector



Fig. 1. Alkylation of biphenyl reactor setup.



Fig. 2. Biphenyl conversion of various zeolites.

(MSD) directly connected to a 6890 GC using the same GC conditions and column as the 6890 Agilent GC-FID. Thus, the retention times and patterns of specific compounds between the two instruments theoretically remain identical.

3. Results and discussion

Typical reaction results for the different zeolite catalysts used in the alkylation of biphenyl with propylene under standard conditions are shown in Fig. 2. HY and amorphous SiO₂/Al₂O₃ catalysts exhibited high initial activity, 90% conversion of biphenyl for HY and around 70% for SiO₂/Al₂O₃ within 5 min of reaction, after which a leveling off was observed within 1 h, as shown in Fig. 2. The conversion of biphenyl was found to increase with reaction time for HZSM-5 and DMOR zeolites, leveling off in approximately 4 h. After a leveling off, HZSM-5 zeolite exhibited 33% conversion, while that of DMOR was much higher at 96%. For comparison untreated mordenite zeolite (HMOR) was also tested and found to be less active than the dealuminated mordenite. The behavior of the zeolites differed somewhat with reaction time. The activity trend of the different catalysts used was as follows: amorphous SiO₂/Al₂O₃ > HY > DMOR > HMOR \gg HZSM-5.

Fig. 3 shows the FT-IR spectra of pyridine adsorbed on the various catalysts. In the region 1400–1570 cm⁻¹, three sharp bands due to the C-C stretching vibrations of pyridine were observed. The band at $1490\,\text{cm}^{-1}$ is due to pyridine adsorbed on both Brønsted and Lewis acid sites, while the bands at 1546 and $1455 \, \text{cm}^{-1}$ are due to the protonated pyridine molecule adsorbed on Brønsted acid sites (B) and Lewis acid sites (L), respectively [26]. Generally, the acidity of a catalyst influences product distribution as well as catalytic activity. In order to understand the relationship between catalytic activity and the acidic properties of a catalyst, we measured band intensity ratio for pyridine adsorbed on Brønsted acid sites and Lewis acid sites respectively, as illustrated in Table 1. The Brønsted to Lewis acid ratios were determined on the basis of the integrated absorbances of the bands at 1546 and 1455 cm⁻¹, respectively. The *L*/*B* acidity ratio was found to be high for amorphous SiO₂/Al₂O₃ and low for HZSM-5 zeolite. Biphenyl conversions for all of the catalysts followed a similar trend as the Lewis to Brønsted (L/B) acidity ratios.



Fig. 3. Pyridine adsorption FT-IR spectra of zeolite catalysts.

3.1. Amorphous SiO₂/Al₂O₃ catalyst

Fig. 4A shows the selectivity of isopropylates for the amorphous SiO₂/Al₂O₃ catalyst. The selectivity of isopropylbiphenyl (IPB) isomers decreased with reaction time. However, the selectivity of diisopropylbiphenyl (DIPB) isomers first increased with time, reached a maximum in 30 min, and then further decreased with time. The formation of triisopropylbiphenyl (TriIPB), tetraisopropylbiphenyl (TetraIPB) and penta isomers were also enhanced with time. The results of silica-alumina catalyst are caused by the large reaction spaces inside the channels. The selectivity of mono and DIPB isomers are shown in Fig. 4B. The initial selectivity of 4-IPB was found to be 37% and it decreased with time, and similar trends were observed in the cases of the 2- and 3-IPB isomers. However, the selectivities of 4,4'-DIPB and 3,4'-DIPB were almost identical and less than 10%. The selectivities of IPB and DIPB of silica-alumina catalyst are shown in Fig. 5A and B, respectively. The selectivity of IPB isomers changed with reaction time. Among the IPB isomers, the selectivities for 4-, 3- and 2-IPB were ca. 50, 25, and 25%, while that of 3-IPB increased with time with corresponding decreases in selectivities of 2- and 4-IPB isomers. 3-IPB is thermodynamically stable among the IPB isomers. These changes are also considered to be due to the isomerization of 4- and 2-IPB to 3-IPB. Among the DIPB isomers, the formation of 4,4'-DIPB and 3,4'-DIPB isomers were obtained only in low selectivities, and thus the formation of the other DIPB isomers (2,2'-, 2,3'-, 2,4'-, and 3,3'-DIPB) were predominant. The selectivities of all the DIPB isomers did not change significantly with reaction time. These features of the catalysis over silica-alumina suggest that their channels have no shape-selective nature for the alkylation of biphenyl with propylene because the reaction spaces inside the channels are too large for the selective formation of 4,4'-DIPB, while it can allow all DIPB



Fig. 4. Selectivity of various isopropylates over amorphous SiO₂/Al₂O₃ catalyst.

isomers to form, including bulky isomers such as 2,2'-, 2,3'-, 2,4'-, 3,3'-, and 3,4'-DIPB.

3.2. HY zeolite

The HY zeolite framework type code is FAU (Faujasite), and it has large pores with three-dimensional zeolite channels with cubic symmetry having 12-m ring openings of 7.4 Å in diameter that provide access to a supercage of diameter 12.4 Å [27]. The selectivities of various isopropylates over HY zeolite catalyst are shown in Fig. 6A and B. Diisopropylbiphenyl isomers are the predominant products, IPB and DIPB selectivities were found to be \sim 22% and 48% respectively; however, no significant changes in selectivity were observed with time. The formation of tri, tetra, and penta isomers was also observed. The selectivity of 4,4'-DIPB in the products over HY zeolite was found to be less than 10%. The sum of other DIPB isomers (2,x') and (3,3') was much higher than this. It was found that, among the mono isopropyl biphenyls, 3-IPB is the dominant isomer. The selectivities for 4-, 3- and 2-IPB were ca. 40, 55, and 5%, and no significant changes in selectivities were observed with time (Fig. 7A). The selectivities of 4,4'-DIPB and 3,4'-DIPB isomers were relatively low (10% and 35%, respectively) and thus the formation other DIPB isomers predominated (Fig. 7B). The selectivities of DIPB isomers were almost constant throughout the reaction. The

results indicate that HY zeolite has no shape-selective nature for the alkylation of biphenyl with propylene because the channels allow for the formation of bulky transition states, even those of bulky DIPB isomers. The alkylation of biphenyl with propylene over HY was accompanied by significant formation of polyisopropylated products, such as triisopropylbiphenyls (TriIPB) and tetraisopropylbiphenyls (TetraIPB). The results support the assertion that HY channels are too large for the selective formation of 4,4'-DIPB.

3.3. HZSM-5 zeolite

The HZSM-5 zeolite framework type code is MFI; it has threedimensional zeolite channels, with a 10-MR pore entrance [27]. The selectivities of various isopropylates over HZSM-5 zeolite catalyst are shown in Fig. 8A and B. IPB isomers are the major products, the selectivity of isopropylbiphenyl (~84%) over HZSM-5 zeolite was found to initially increase and then slightly decrease with time, whereas the selectivity of DIPB slightly increased with time, reaching a maximum value of 10% (Fig. 8A). Another interesting feature of the catalyst is that the formation of higher isopropylates was not observed. The selectivities of individual isomers are shown in Fig. 8B, the selectivity of 4-IPB isomer being the highest among the products and 4,4'-DIPB selectivity being very low (i.e., <5%). It was found that among the mono isopropyl biphenyls 4-IPB is



Fig. 5. Selectivity of IPB and DIPB isomers over amorphous SiO₂/Al₂O₃ catalyst.



Fig. 6. Selectivity of various isopropylates over HY zeolite.



Fig. 7. Selectivity of IPB and DIPB isomers over HY zeolite.

the predominant one (Fig. 9A). The selectivities for 4-, 3- and 2-IPB were ca. 55, 33, and 12%, and the selectivities were constant throughout the reaction. Among the DIPB isomers, the selectivities of 4,4'-DIPB and 3,4'-DIPB isomers were found to be 34% and 23%, respectively. The selectivities of all the DIPB isomers remained relatively constant with reaction time. These features of the catalysis over HZSM-5 suggest that their channels have no shape-selective nature for the alkylation of biphenyl with propylene, because the



Fig. 8. Selectivity of various isopropylates over HZSM-5 zeolite.



Fig. 9. Selectivity of IPB and DIPB isomers over HZSM-5 zeolite.

ZSM-5 channels are too small for the selective formation of 4,4'-DIPB, they cannot allow the DIPB isomers to form including even the least bulky isomer, such as 4,4'-DIPB. Hence, the formation of mono alkylated biphenyls predominated.

3.4. Dealuminated mordenite (DMOR) zeolite

Mordenite belongs to the category of zeolites having orthorhombic symmetry, with a pore structure that is effectively one-dimensional. Elliptical straight channels of 12-MR pore entrances $(6.5 \text{ Å} \times 7.0 \text{ Å})$ run parallel to the [001] direction and have small side pockets $(2.6 \text{ Å} \times 5.7 \text{ Å})$ parallel to the [010] direction, which connect to the next 12-m channel. Dealumination is an important method for the enhancement of catalytic performance of mordenite, because it results in a decrease in acid sites and an increase in mesoporosity. The selectivities of IPB isomers decreased with reaction time, whereas the selectivity of DIPB isomers increased monotonically with reaction time. Another interesting feature of the catalyst is that the formation of higher isopropylates was low (i.e., less than 3%), which is shown in Fig. 10A. Fig. 10B shows a typical profile for the alkylation of biphenyl with propylene over DMOR under 1 MPa of propylene pressure. At an early stage of the reaction, biphenyl is converted into IPB isomers, and especially 4-IPB. At the same time the selectivity of DIPB isomers increased with time, especially toward

the formation of 4,4'-DIPB. The yield of 4-IPB reached a maximum at 60% conversion, and then, decreased at higher conversion. However, the yield of 3-IPB slightly increased with the conversion, although its formation leveled off at high conversion (Fig. 11A). This shows that 4-IPB was much more reactive than 3-IPB for the formation of DIPB isomers. The yields of 4,4'-DIPB and 3,4'-DIPB increased linearly with increasing total DIPB yield during the reaction, as shown in Fig. 11B. The yield of DIPB isomers, and especially 3,4'- and 4,4'-DIPB, increased with the consumption of 4-IPB. The formation of 4,4'-DIPB was highly selective, and the selectivity was almost constant throughout the course of the reaction. Fig. 12 shows the yields of 3-IPB, 4IPB, 3,4'-DIPB and 4,4'-DIPB of untreated mordenite (HMOR) zeolite. HMOR also followed the same trends in yields with DMOR, whereas the percentages of yields are lower relative to dealuminated mordenite.

It was found that among the mono isopropyl biphenyls, 4-IPB is the predominant one (Fig. 13A). In the early stages of the reaction, the selectivities for 4-, 3- and 2-IPB were ca. 82, 17, and 1%. The selectivity of 4-IPB was found to decrease with reaction time, and the corresponding 3-IPB selectivity gradually increased. Finally, after conversion reached a leveling off, both 4-IPB and 3-IPB reached the same selectivity, due to the 3-IPB being the thermodynamically more stable isomer. The formation of 4,4'-DIPB predominates among the DIPB isomers, and it has 90% selectivity, while 3,4'-DIPB and other DIPB isomers had very low selectivities



Fig. 10. Selectivity of various isopropylates over DMOR zeolite.



Fig. 11. Effect on IPB yield and DIPB yield over DMOR zeolite.



Fig. 12. Effect on IPB yield and DIPB yield over HMOR zeolite.

(Fig. 13B). The selectivity of 4,4'-DIPB isomer slightly decreased with time, while the corresponding 3,4'-DIPB selectivity slightly increased. The decrease in the selectivity for 4,4'-DIPB is due to the isomerization to thermodynamically stable 3,4'-DIPB on external acid sites of MOR. These results indicate that the dealuminated

mordenite channels are appropriate for shape-selective formation of 4,4'-DIPB. The time-on-stream (TOS) analysis against activity for the alkylation of biphenyl reaction over dealuminated MOR zeolite was carried out for a continuous period of 30 h and the results are represented in Fig. 14. It is evident that dealuminated MOR



Fig. 13. Selectivity of IPB and DIPB isomers over DMOR zeolite.



Scheme 1. Alkylation of biphenyl with propylene reaction pathway.

zeolite exhibits better stability with a period of 30 h. However the selectivity of 4,4'-diisopropylbiphenyl decreased with time and the corresponding selectivity increased for of 3,4'-diisopropylbiphenyl (not shown), which might be due to the isomerization of 4,4'-diisopropylbiphenyl on external acid sites.

Figs. 10 and 13 reveal that shape-selective alkylation of biphenyl with propylene occurs to yield, predominantly, the least bulky 4-IPB among IPB isomers and 4,4'-DIPB among DIPB isomers. 4,4'-DIPB is produced by the consumption of 4-IPB, leading to the accumulation of 2-IPB and 3-IPB. The high selectivity of 4,4'-DIPB among the other DIPB isomers suggests that alkylation of biphenyl with propylene proceeds through a consecutive reaction mechanism via 4-IPB, as shown in Scheme 1; in the first stage of the reaction biphenyl is predominantly converted to form IPB isomers as governed by the shape-selectivity of the mordenite pore to yield 4-IPB as the principal isomer (Fig. 10A), which yields 4,4'-DIPB by further alkylation of biphenyl with propylene. 3,4'-DIPB and 3,3'-DIPB were also formed by the isomerization of 4,4'-DIPB as side products. 4-IPB is a precursor to produce 4,4'-DIPB, but 3-IPB does not participate significantly in the formation of 3,4'-DIPB, except at a late stage, because it is a bulkier isomer than 4-IPB. No further alkylation of 4,4'-DIPB to tri, tetra and penta isomers was observed



Fig. 14. Effect of the stability of the DMOR catalyst for alkylation of biphenyl reaction with respect to time-on-stream.

even at 300 C. This is because there is not enough space in the mordenite pores for the transition state of further alkylation of 4,4'-DIPB. Selectivity for 4,4'-DIPB is high with mordenite among all these zeolite, due to the bulky isomers being prohibited by these channels, whereas, HY and SiO₂/Al₂O₃ channels are too large for the elimination of bulkier isomers. HZSM-5 channels are too small to accommodate such a large product molecules. These findings for HY, HZSM-5 and DMOR indicate that the geometry of the zeo-lite channels is very important for the shape-selective formation of 4,4'-DIPB.

4. Conclusions

The reaction of alkylation of biphenyl with propylene has been studied on HY, HZSM-5, DMOR, HMOR zeolites and amorphous SiO₂/Al₂O₃ catalyst. The catalytic activity of the reaction follows the order: amorphous SiO₂/Al₂O₃ > HY > DMOR > HMOR \gg HZSM-5. Lewis to Brønsted (*L*/*B*) acidity ratios were found to be high for amorphous SiO₂/Al₂O₃ and low for HZSM-5 zeolite. A 96% conversion of biphenyl and 90% selectivity of 4,4'-DIPB was obtained over dealuminated mordenite zeolite, even at temperatures as high as 300 °C. Highly shape-selective alkylation of biphenyl with propylene was achieved over DMOR zeolite. The selectivity for 4,4'-DIPB is high for dealuminated mordenite zeolite, whereas for HY, HZSM-5 and amorphous SiO₂-Al₂O₃ the selectivity was very low and in the range of 10–35%. These results show that the shape-selective catalysis of zeolites in the alkylation of biphenyl with propylene is governed by the geometry of the channels and pore entrances.

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