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Alkylation of biphenyl with propylene using acid catalysts

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Abstract

Alkylation of biphenyl with propylene was carried out over various zeolites such as HY, H-ZSM-5, Beta, MCM-22, SSZ-25 and SSZ-26. The influence of zeolite structure on reaction activity and selectivity was studied. The alkylation activity follows the order: Y > Beta ≈ SSZ-26 > MCM-22 > SSZ-25 > ZSM-5. The influence of framework Si/Al ratio and crystal size for the tri-directional 12 member ring structures (Y and Beta) has been studied and it has been observed that, under the reaction conditions used here, the process is not diffusion controlled. High selectivity to *ortho*-isopropylbiphenyl (*o*-IPBP) was obtained using MCM-22 and SSZ-25 zeolites, both with a MWW structure. The high *o*-IPBP selectivity as well as the differences observed between the two zeolite samples have been explained on the bases of differences in crystal size and assuming that on this zeolite structure the reaction only takes place on the external surface.

Keywords: HY zeolite; Beta; MCM-22; SSZ-25; SSZ-26; Alkylation of biphenyl; Propylene; Activity; Shape selectivity

1. Introduction

The Friedel–Crafts alkylation of aromatics using zeolites has been extensively studied from basic and applied points of view in order to introduce functional groups in aromatic hydrocarbons [1–5]. More specifically, the alkylation of biphenyl with propylene is a reaction of practical interest since it may produce 4,4′-diisopropylbiphenyl (4,4′-DIPB) [6–18], an important intermediate in the preparation of thermotropic polymers of use in liquid crystal manufacture [19,20]. Problems in the industrial process of 4,4′-DIPB manufacture like corrosivity, toxicity and production of pollutants, make convenient to change the traditional $AlCl_3$ or $FeCl_3$ catalysts by acid solid catalysts.

Previous studies [6–18] have pointed out that the H-mordenite is a selective catalyst to produce *para*-alkyl compounds. Unfortunately, this zeolite is rapidly deactivated by coke deposition [11–18,21] and, several studies have been directed to enhance the performance of mordenite catalysts modifying zeolite parameters such as the framework Si/Al ratio [13–15], the Na exchanged level by either protons [16] or rare earth cations [17]. Other materials such as SAPO-11 [18], pillared clays [21–24], and zeolites such as ZSM-5, ZSM-12 [25], have been also studied in this reaction, but results are similar or poorer than with the mordenite. Correlations between activity and selectivity with the pore structure, the framework Si/Al ratio, the degree of dealumination and the ratio of internal/external active site have been established [10–14,25].

The majority of the studies of the catalytic alkylation of biphenyl with propylene has been made in liquid phase bath reaction systems, and very few [22–25] have studied this reaction in gas phase. Butruille

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et al. [22–24] compared the catalytic performance of different aluminium pillared clays and zeolites such as USY and H-mordenite. They found a relationship between the microporosity of the pillared clays and the selectivity to *meta*- and *para*-monolakylated isomers. Loktev and Chekriy [25] studied this reaction over zeolites Y, Beta, mordenite, ZSM-5 and ZSM-12. They related the activity and selectivity of the catalysts with their pore structures and concluded that the constraint effects as present in mordenite and ZSM-12 zeolites are needed to obtain a high selectivity to 4,4′-diisopropylbiphenyl.

In the present paper, the alkylation of biphenyl with propylene over zeolites with different pore structures has been studied in gas phase using a continuous flow reactor system. Different zeolites have been used, including recently described materials such as MCM-22, SSZ-25 and SSZ-26. The effect of acid strength and density, crystal size, and pore dimensions and topology on the catalytic activity and selectivity has been evaluated.

2. Experimental

2.1. Materials

Four HY zeolite catalysts with different framework Si/Al ratios, named as HY(PQ)-*i* ($i = 1$, 2, 3, 4) have been used in this paper. They have been prepared from different commercial Y zeolites CBV-100 (NaY, Si/Al = 2.6), CBV-500 (NH_4Y, Si/Al = 2.6) and CBV-720 (HY, Si/Al = 15), all of them from PQ Zeolites B.V. The morphology of these zeolites is the same and consists of agglomerates of different sizes (2–6 μm) composed by small crystallites of 0.4–0.6 μm. HY(PQ)-1 was prepared from CBV-500 by calcination in vacuum at 773 K for 3 h. HY(PQ)-2 was prepared from CBV-500 by steaming at 800 K for 4 h. HY(PQ)-3 was prepared from CBV-100 by three NH_4Cl exchanges (2.5 M, 353 K, 1 h), calcining at 823 K for 3 h and steaming at 923 K for 3 h. HY(PQ)-4 is the untreated CBV-720.

Three Beta zeolites, Beta-1, Beta-2 and Beta-3, have been prepared in our laboratory [26] with controlled crystal sizes of 0.9, 0.3, and 0.056 μm, respectively, and similar framework Si/Al ratio. The acid form of these samples was obtained by carrying out three times the NH_4^+ exchange and calcination, in the same way than HY(PQ)-3. The rest of zeolites used in this study comes either from PQ Zeolites B.V. (ZSM-5), or they were prepared in our laboratory (MCM-22, SSZ-25 and SSZ-26) [27–29] and transformed in the acid form by several NH_4^+ exchanges with intermediate calcination steps.

The reactants employed were: biphenyl (99.9% from Sigma), propylene (99.99 % from Abello), heptane as solvent (99.0% from Sharlau), and nitrogen as diluent gas (99.9%).

2.2. Reaction

The alkylation of biphenyl with propylene was carried out in a continuous, fixed bed, glass tubular reactor electrically heated. The temperature of reaction was 523 K. Biphenyl was diluted in heptane (20 wt.%) and the mixture was fed into the reactor together with propylene being the ratio of biphenyl to propylene 5 mol mol^{-1} when using HY and HZSM-5 catalysts and 4 mol mol^{-1} for the other catalysts. Samples of reaction products were collected at different times on stream, and analyzed by gas chromatography. The contact time was changed for the different catalysts by changing the amount of catalyst and maintaining constant the flow of feed (1.36 mol/h of biphenyl).

2.3. Catalyst characterization

The crystallinity of the HY zeolites was calculated by X-ray diffraction by comparing the area of the (5,3,3) peak and considering the crystallinity of the CBV-100 sample as 100% crystalline. The unit cell size of the HY samples was determined by X-ray diffraction using the Cu Ka radiation according to the ASTM D-3942–80 procedure. The estimated standard deviation was ±0.01 Å, and the framework Si/Al ratio was calculated using the Fichtner–Schmittler equation [30]. The crystal size of the zeolites was measured by SEM.

The crystallinities of Beta, MCM-22, ZSM-5, SSZ-25 and SSZ-26 zeolites were calculated by comparing the area of at least three peaks of the sample diffractograms with the most crystalline standard of each material available in our laboratory.

Table 1
Physicochemical properties of the catalysts

Catalyst	Crystal size (μm)	Framework Si/Al	Crystallinity (%)	mmol py/g_{cat} after desorption at		
				523 K	623 K	673 K
HY(PQ)-1	2–6[a]	4.38	93	127	38	14
HY(PQ)-2		5.16	95	90	45	24
HY(PQ)-3		7.24	87	76	31	14
HY(PQ)-4		18.61	78	57	24	14
H-ZSM-5	1–3	20.3	79			
H-Beta-1	0.9	15.0	77	18	6	3
H-Beta-2	0.3	16.0	79	27	14	6
H-Beta-3	0.056	18.0	78	27	18	7
H-MCM-22	0.2	28.4	86	29	19	7
H-SSZ-25	0.7	27.0	93	62	30	17
H-SSZ-26	1.0	19.0	100	50	33	19

[a] Agglomerates composed by small crystallites of 0.4–0.6 μm.

Infrared spectroscopic measurements were carried out in a conventional greaseless I.R. cell using a FTIR Nicolet 710. Self-supported wafers of $10\,mg\,cm^{-2}$ were pretreated overnight at 773 K and 1.33×10^{-3} Pa of dynamic vacuum. For the pyridine adsorption experiments, 6.6×10^2 Pa of pyridine were introduced into the cell at room temperature. After equilibration the samples were outgassed at different temperatures (from 523 to 723 K) under vacuum and the spectra recorded at room temperature.

The textural characteristics of the zeolites have been determined from the nitrogen adsorption–desorption results (ASAP 100-V-1.04). The main physicochemical and textural characteristics of the catalysts used in this study are resumed in Tables 1 and 2.

Table 2
Textural properties of the catalysts

Catalyst	Surface area (m^2/g)	Micropore volume (cm^3/g)
HY(PQ)-1	537	0.234
HY(PQ)-2	569	0.245
HY(PQ)-3	577	0.247
HY(PQ)-4	627	0.234
H-ZSM-5	396	0.109
H-Beta-1	460	0.185
H-Beta-2	583	0.187
H-Beta-3	554	0.181
H-MCM-22	356	0.129
H-SSZ-25	468	0.177
H-SSZ-26	541	0.213

3. Results and discussion

3.1. Catalytic activity

Similarly as it occurred during the gas phase catalytic alkylation of biphenyl with methanol with different zeolites [31], the activity decreases with time on stream on all the catalysts studied due to the formation of coke on the catalyst surface. As an example, the variation of total conversion of biphenyl with time on stream for two of the catalysts (H-Beta-1 and H-MCM-22) is shown in Fig. 1a and b.

In order to compare the catalytic activity of the samples in absence of deactivation, the biphenyl conversion at time on stream zero was estimated from the values of conversion obtained at different times on stream and fitting these conversions to the following equation:

$$x_t = x_0 \exp\left[-k_d\, dt^{0.5}\right] \quad (1)$$

where x_0 is the conversion at zero time on stream and x_t is the conversion at a given time on stream, t is the time on stream and k_d is a decay constant. In all cases a good fitting of Eq. (1) to the experimental data has been observed.

The reaction was followed at different contact times for each catalyst samples, and from the results obtained under differential reactor conditions at zero time on stream the initial reaction rates were calculated. These values together with the decay constants are shown in Table 3. As can be seen in this Table,

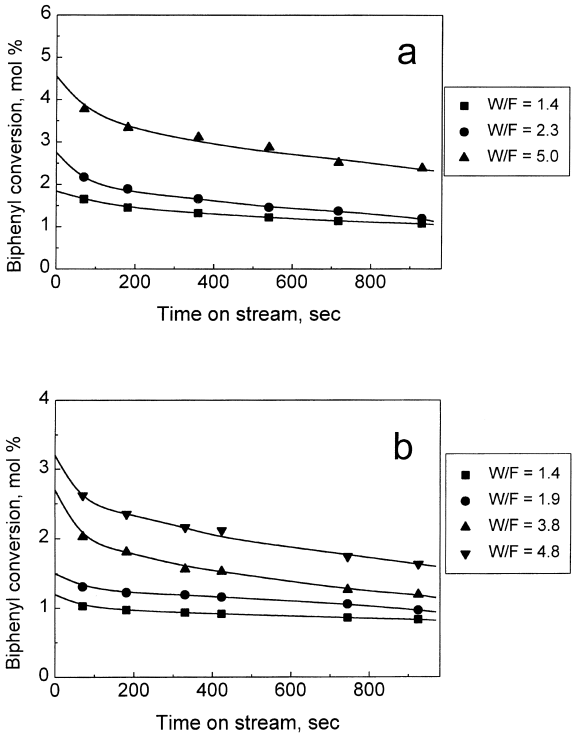

Fig. 1. Total conversion vs. time on stream in the alkylation of biphenyl with propylene at 523 K and different contact times on H-Beta-3 (Fig. 1a) and H-MCM-22 (Fig. 1b) zeolites.

while the calculated deactivation constants change, in some cases, with total conversion, it is possible nevertheless to establish the following order of deactivation: HY(PQ)-*i* > HZSM-5 > H-Beta-*i* ≥ H-MCM-22,

Table 3
Deactivation constant and reaction rate for the reaction at 523 K

Catalyst	Total conversion (%)[a]	$k_d \times 10^3$ ($s^{-1/2}$)[b]	Reaction rate (mol/g h)
HY(PQ)-1	5–9	32–33	0.100
HY(PQ)-2	6–11	37	0.122
HY(PQ)-3	4–8	36–38	0.085
HY(PQ)-4	3–9	30	0.071
H-Beta-1	2–5	15–25	0.009
H-Beta-2	3–7	16–22	0.019
H-Beta-3	3–8	15–24	0.023
H-ZSM-5	0.1–0.4	25–27	0.0019
H-MCM-22	1–3	12–26	0.0077
H-SSZ-25	1–3	12–22	0.0060
H-SSZ-26	3–9	10–21	0.020

[a] Experimental range of biphenyl conversion (molar %).
[b] Range of calculated deactivation constants.

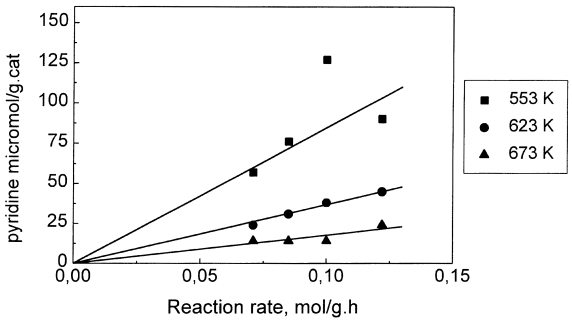

Fig. 2. Correlation between initial reaction rates at 523 K and pyridine retained on catalysts after desorption at different temperatures: (a) 553, (b) 623, and (c) 673 K, in the series of HY(PQ) catalysts.

H-SSZ-25, H-SSZ-26. It can be seen that there is not a direct correlation between deactivation rate and catalytic activity.

3.1.1. Influence of zeolite composition on catalytic activity

The initial reaction rate for the HY zeolites (Table 3) increases when increasing the framework Al content until reaching a maximum on the HY(PQ)-2. After this point, an increase of the framework Al content of the zeolite produces a decrease on the initial reaction rate. These results indicate that either not all the Brönsted acid sites associated to the framework Al are active for the alkylation of biphenyl with propylene, or not all the framework Al are compensated by protons. The fact that the maximum in activity corresponds to the sample with a higher amount of Brönsted acid sites, as measured by pyridine desorption at higher temperatures, supports the hypothesis that not all the Brönsted sites present on the HY samples are active, but only those retaining pyridine at desorption temperatures ≥623 K. As it is shown in Fig. 2, a linear correlation can be observed between initial reaction rate and pyridine amount retained in the zeolite after desorption at 623 K or higher. In other words, the weaker Brönsted acid sites are not able to catalyze the alkylation reaction, and they are probably better suited to catalyze the competitive olefin oligomerization reaction. Thus, taking into account previous studies [31–34], we can associate the Brönsted sites active for the alkylation of biphenyl with propylene, with those bridging hydroxyl groups related with frame-

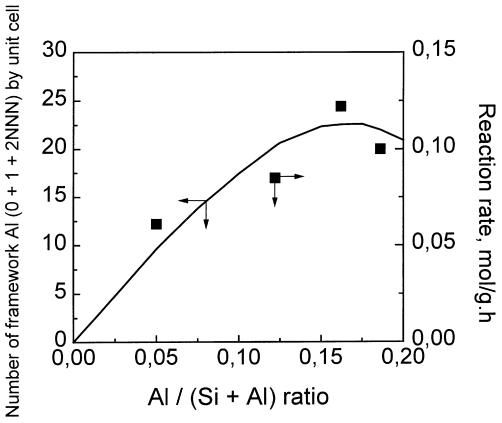

Fig. 3. Correlation between initial reaction rates at 523 K and theoretical number or framework Al with 0, 1 or 2 Al in the second coordination sphere (0NNN + 1NNN + 2NNN) by unit cell in the series of HY(PQ) catalysts.

work Al with 0, 1 or 2 Al in the second coordination sphere (Fig. 3).

When the H-Beta zeolites, in where all Al are presumably isolated, were tested, it can be seen that in agreement with the acidity measured by the pyridine the initial rate on Beta is lower than on HY zeolites. The fact that with similar framework Si/Al ratio the H-Beta has a much lower amount of Brönsted acid sites measured by pyridine adsorption–desorption clearly indicates, regardless of differences in unit cell dimensions, that a large number of Brönsted acidity was lost during the calcination process, probably due to the partial dealumination of the Beta zeolite. Nevertheless, taking into account the smaller pore diameter of Beta zeolite one can be also suppose that differences in activity may be due to diffusional limitations of the reactants or products in the case of the BEA structure. In order to study this, the crystal size of Beta was changed while keeping constant the composition. While an increase in activity is obtained when decreasing the crystallite size, which may be an indication of diffusion control, the differences in activity are directly related with the number of the stronger active sites, and it is known that pyridine has not diffusion limitations in the BEA structure. It can be concluded without ambiguities that Brönsted acid sites with medium and strong strengths are active for the alkylation of biphenyl with propylene.

3.1.2. Influence of zeolite structure on activity

In the case of ZSM-5 and MWW (MCM-22 and SSZ-25) structures, the presence of 10 member ring (MR) channels or windows introduces strong constraints for biphenyl to diffuse into the channels. Thus, in this case, the pyridine which can diffuse into the 10 MR channels is not a good probe to measure the amount of accessible acid sites. Then, it is assumed that with ZSM-5 and MWW structures, only the external surface will be active for carrying out the reaction. In this case, the crystallite size will be the determinant factor on activity, and this is indeed seen from the results given in Tables 1 and 3.

The SSZ-26 presents an interesting structure formed by 12 and 10 MR channels which cross. In this structure, the reactant can probably diffuse through the 12 MR openings and in this way can travel through the structure. However, the presence of the 10 MR openings will reduce the possibilities of diffusion in the direction involving 10 MR window [35]. Then, one can expect that if biphenyl can diffuse in this structure, the diffusion coefficient will be smaller than in the tri-directional 12 MR Y and Beta zeolites. This is indeed observed when considering the acidity and activity results given in Tables 1 and 3.

3.2. Catalytic selectivity

The yields to the different products obtained in the reaction of alkylation of biphenyl have also been determined at zero time on stream in order to avoid the possible influence of catalyst deactivation on selectivity. As expected, the main primary products observed are: *o*-, *m*- and *p*-isopropylbiphenyls (IPBP), while diisopropylbiphenyls (DIPB) appear as secondary products on all catalysts. No other products than IPBP or DIPB were detected with our analytical system (see as an example the results given in Fig. 4).

In Fig. 5a–d, the influence of total conversion on reaction product selectivities for some of the catalysts are shown. In these Figures, the selectivities to *o*-, *m*-, and *p*-IPBP are referred to the total yield of monoalkylated products. In all cases, the selectivities of the three monoalkylated biphenyls do not change with total conversion. Otherwise, the selectivity to DIPB increases with total conversion as can be expected for a secondary reaction.

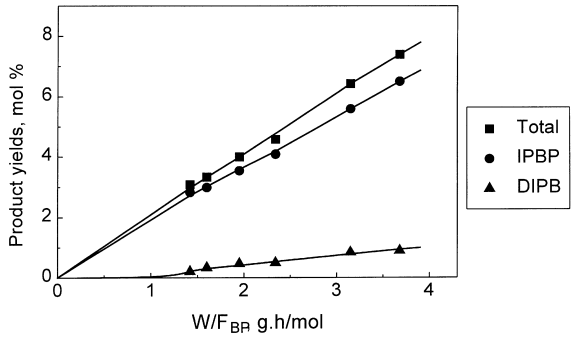

Fig. 4. Total conversion and IPBP and DIPB yields vs. contact time, W/F_{BP} (g h/mol) in the alkylation of biphenyl with propene on H-Beta-2 catalyst at 523 K.

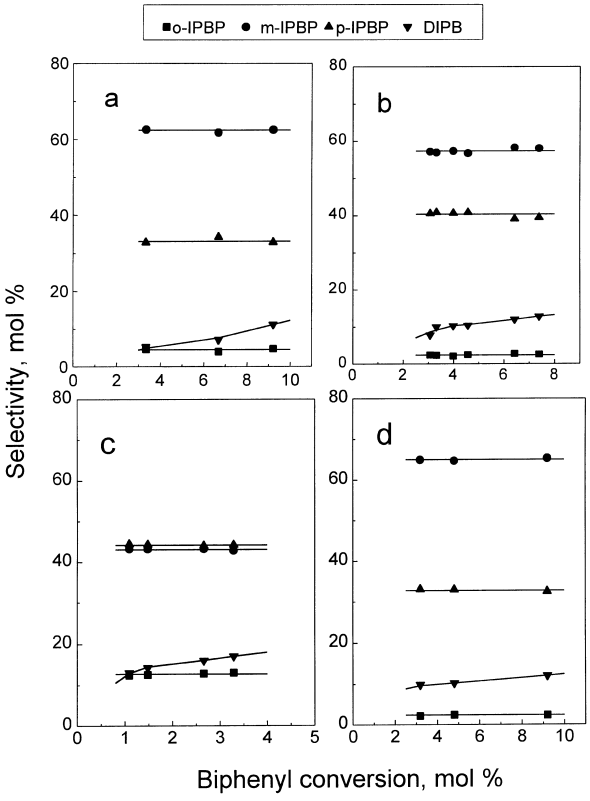

Fig. 5. Selectivity of *o*-IPBP, *m*-IPBP, *p*-IPBP and DIPB vs. total conversion in the alkylation of biphenyl with propene on several zeolites at 523 K. (a) on HY(PQ)-4 sample; (b) on H-Beta-2 sample; (c) on H-MCM-22 sample; and (d) on H-SSZ-26 sample.

Table 4
Selectivity of reaction products ($T = 523$ K, biphenyl conversion ~ 4%)

Catalyst	Product selectivities (mol%)				
	IPBP	DIPB	*o*-IPBP	*m*-IPBP	*p*-IPBP
HY(PQ)-1	94.8	5.2	3.1	62.5	34.4
HY(PQ)-2	94.5	5.5	5.1	60.9	34.0
HY(PQ)-3	91.4	8.6	4.2	63.2	32.6
HY(PQ)-4	93.6	6.4	4.5	61.4	33.1
H-ZSM-5[a]	100.0	0.0	0.0	0.0	100.0
H-Beta-1	85.6	14.4	2.6	57.0	40.6
H-Beta-2	89.7	10.3	2.4	57.3	40.3
H-Beta-3	89.5	10.5	0.0	52.5	47.5
H-MCM-22	82.0	18.0	12.7	43.1	44.2
H-SSZ-25	78.0	22.0	9.2	43.9	46.9
H-SSZ-26	90.0	10.0	2.3	65.0	32.7

[a] Biphenyl conversion = 0.4%.

Table 4 summarizes the selectivities observed on the different catalysts at the same total conversion (~4%), except for H-ZSM-5 sample for which the total conversion is 0.4%. The selectivities to the three IPBP isomers have also been referred to the total IPBP yield. In this way, we can compare the formation of the different isomers can be compared independently of the total selectivity to monoalkylated products.

As can be seen in Table 4, no significative influence of framework Si/Al ratio of HY(PQ) samples on reaction product selectivities has been observed. This is an indication that the density of active sites and their acid strength distribution do not have an important influence in the product selectivities which only depend of the zeolite structure.

H-ZSM-5 zeolite selectively produces *p*-isopropylbiphenyl, the small size of its pores avoids the formation of bulkier *o*-. and *m*-IPBP, and also the formation of DIPBs. Strong diffusion restrictions on this zeolite also explain the low catalytic activity found.

For H-Beta zeolites (Table 4), the selectivity to *o*-IPBP is lower than the corresponding selectivity for HY(PQ) zeolites and this selectivity decreases when zeolite crystal size increases. The *o*-IPBP is the bulkiest isomer, it has a kinetic diameter of 7.5 Å in a twisted bulky conformation with an angle of 64° [36]. Then, H-Beta zeolites present higher selectivity to form *m*- and *p*-IPBP which have less sterical impediments. The influence of crystal size of H-Beta samples on product distributions and also, as it is indicated before, on the catalytic activity indicate that some

diffusion control on product distribution is present in these zeolites.

H-MCM-22 zeolite shows a very high selectivity of *o*-IPBP, higher than obtained for HY(PQ) zeolites. As it is said before, the access to the supercages in H-MCM-22 is restricted to 10 MR windows of about 5.2 Å in diameter. It is very difficult to think that *o*-IPBP formed in supercages can be passed trough these windows. Then, the formation of *o*-IPBP in this zeolite has to be limited to the active sites in external surface.

H-SSZ-25 zeolite, isostructural form to the MCM-22, also shows a high selectivity of *o*-IPBP, but lower than H-MCM-22 zeolite. This result can be explained considering the differences in external surface of these zeolites due to the respective differences in the crystal sizes (Table 1). The supposition that the alkylation reaction on these zeolites is limited to the external surface also explain the high selectivity to DIPBs observed (higher than for HY(PQ) zeolites) and the low reaction rate obtained (Table 3). The products distribution obtained with H-SSZ-26 indicates that the alkylation reactions occur in the pores of the zeolite and, similarly to the H-Beta zeolites, a diffusion control of bulkier isomers, as *o*-IPBP, can explain the results.

4. Conclusions

The reaction of alkylation of biphenyl with propylene has been studied on different microporous zeolites. The catalytic activity of the reaction follows the order: HY(PQ) > H-Beta ∼ H-SSZ-26 > H-MCM-22 > H-SSZ-25 > H-ZSM-5. This reaction is catalyzed by strong Brönsted acid sites (which retain adsorbed pyridine at desorption temperature of 623 K or higher). The catalytic activity and selectivity of the studied zeolites can be explained taking into account the zeolite structure and the accessibility of molecules. For zeolites with pore sizes equal or lower than Beta zeolite a diffusion control of the reaction exists that it has an influence on the catalytic activity and the product distribution obtained. However, H-MCM-22 and SSZ-25 zeolites show a very high selectivities of *o*-IPBP and DIPBs, that cannot be explained by their pore structures. The accessibility of the internal surface in these zeolites is limited by 10MR channels which connect the supercages with the exterior, and the catalytic activity and selectivity for these zeolites can be explained if the reaction mainly occurs on the external surface of the crystals. This hypothesis can also explain the observed differences in activity for these two zeolites, which can be attributed to the different crystal sizes and corresponding external surface areas of the two zeolites. The catalytic activity could seem very high supposing that the reaction mainly occurs on the external surface area. If it is so, these zeolites may have a considerable external surface area, and it can be possible taking into account the structures of these zeolites. Roque-Malherbe et al. [37] studied the diffusion of aromatic hydrocarbons in several zeolites. In the case of MCM-22 zeolite they found two superimposed processes (one very rapid and the other very slow) in the diffusion of a bulky molecule as *o*-xylene, and they attributed the rapid diffusion of *o*-xylene to the presence of the truncated cavities on the external crystal face in the [0 0 1] direction. Then, a significant amount of active sizes, but no selective sites, can be directly accessible to the reactants, being responsible to the higher DIPB selectivity and the distribution of the monoalkylated isomers for these zeolites.

The reaction of alkylation of biphenyl with propylene on zeolites can be considered a clean reaction to obtain only alkylated products, without other lateral reactions, and it can be used as a test reaction to characterize large and medium pore zeolites. It is important to compare catalytic activity and selectivity in absence of deactivation to be sure to obtain the appropriate values.

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