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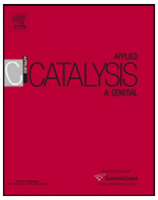

Benzylation of benzene with benzyl alcohol on zeolite catalysts

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ABSTRACT

The catalytic liquid phase benzylation of benzene to diphenylmethane (DPM) with benzyl alcohol (BnOH) was investigated over various zeolite catalysts (HSZ 600 mordenite, CBV 20A mordenite, H-beta zeolites with Si/Al of 10.8 and 35.8, respectively) at 353–423 K and under atmospheric pressure, using three reaction methodologies: (A) by adding all benzyl alcohol at the beginning of the reaction, (B) by dropwise addition of benzyl alcohol (1–2 drops/min for 4 h) and (C) under continuous flow conditions. Nafion-embedded silica and $AlCl_3$/MCM-41 were also tested for comparison. The conversion and product distribution largely depended on the experimental conditions and the zeolite nature. Under optimal conditions using the Beta zeolite (Si/Al molar ratio of 10.8) and the (C) methodology, selectivity to DPM of 88.9% for a conversion of BnOH of 99.2% were achieved. Recycling tests showed that the catalyst preserved its activity and selectivity to DPM after several cycles.

1. Introduction

Friedel-Crafts alkylation is a very important reaction of organic chemistry that is used for the production of a large variety of chemicals for a wide range of industrial segments. Among these chemicals, benzylated aromatics (an important class of alkylated aromatics) occupy an important place because they are widely used in the large-scale synthesis of petrochemicals, cosmetics, dyes, pharmaceuticals and in many other chemical industries. The benzylation reactions are usually done in liquid phase with homogeneous acid catalysts such as $FeCl_3$, $AlCl_3$, BF_3, $ZnCl_2$, HF, H_2SO_4 and with alkyl halides as alkylating agents [1–3].

Among typical criticisms addressed to homogeneous catalysis (e.g., the difficult separation and recovery of the catalytic species from the reaction medium) drawbacks like disposal of the spent catalyst, corrosion or high toxicity are maybe the most important ones that should obey the environmental legislation. In the last years, to overcome these problems, synthetic organic reactions and especially those for fine and specialty chemicals industries are carried out with Lewis and Brønsted solid acid catalysts [4].

An important chemical compound obtained through the benzylation of benzene is diphenylmethane which is mostly used in the fragrance industry and agrochemicals (Scheme 1). Diphenylmethane is also recommended as a plasticizer to improve the dying properties, as solvents for the dyes and as a dyes carrier printing with disperse dyes. Moreover, the addition of diphenylmethane to saturated linear polyesters improves their thermal stability and its addition to jet fuels increases the stability and lubricating properties [5].

Taking into account the large utilization of this valuable compound, on one hand, and the drawbacks of conditions this is usually prepared, on the other hand, the optimization of the reaction system in the sense of the identification of cheap heterogeneous active catalysts and best experimental conditions is very important. The use of heterogeneous catalysts for this synthesis has already been reported using benzyl chloride or benzyl alcohol as alkylating agent. For example, several solid acid catalysts, such as Fe-modified ZSM-5 and H-beta zeolites, Fe_2O_3-, $FeCl_3$-, In-, Ga, and Zn-deposited or included in micro-, meso- and macro-porous supports, H-beta, H-Y, H-ZSM-5 zeolites, hydrotalcites, $FeCl_3$, $MnCl_2$, $CoCl_2$, $NiCl_2$, $CuCl_2$, or $ZnCl_2$ supported on acidic alumina and Cu-, Ga-, Sn-, Zn-, or supported on mesoporous materials (HMS-n) have been proposed as being active using benzyl chloride as alkylating agent [6–17]. However, a disadvantage of this reaction is the formation of HCl as by-product. Commonly, the use of benzyl alcohol instead of benzyl chloride requires a stronger acid catalyst, as Amberlyst-15, niobic acid or niobium pentoxide, niobium phosphate, metal triflates supported on MCM-41, SBA-15 mesoporous aluminosilica, metal modified zeolites and Nafion-H [18–28]. The reaction proceeds via an electrophile intermediate, which involves the reaction of benzyl alcohol with the acid sites. The Brønsted acid sites polarize the benzylating agent and in turn produces an electrophile ($C_6H_5CH_2^+$). Then the generated electrophilic species attack the benzene ring, resulting in the formation of DPM [29,30].

Here we report a useful reaction methodology for enhancing the selectivity to diphenylmethane in the presence of cheap zeolites

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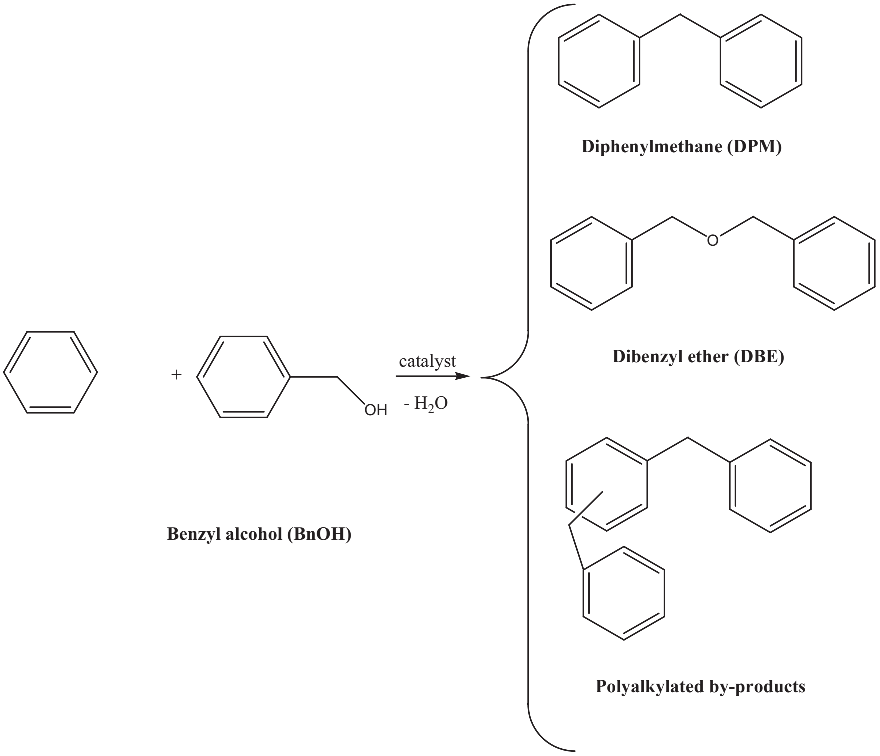


Scheme 1. Friedel-Crafts benzylation of benzene with benzyl alcohol.

(e.g., beta zeolites and mordenates) and environmentally friendly benzyl alcohol as alkylating agent.

2. Experimental

The commercial zeolites with different structures and chemical compositions were purchased from different companies. Therefore, large pore mordenite (HSZ 600) with Si/Al of 3.0, was purchased from TOSOH Company, mordenite CBV 20A with Si/Al of 10.0, was purchased from Zeolyst International, while two H-beta zeolites with Si/Al of 10.8 (PQ25) and 35.8 (PQ75), respectively, were received from PQ-Valfor Company. For comparison they were also used SAC-13 (Nafion-embedded silica) and $AlCl_3$/MCM-41. SAC-13 was purchased from Aldrich (S_{sp} = 400 m^2/g; D_p = 10 nm; V_p = 0.6 mL/g; stable to 473 K, 0.15 mequiv./g, $H_0 \geq -12$ (96% H_2SO_4)). $AlCl_3$-grafted onto MCM-41 was prepared by reacting anhydrous $AlCl_3$ with Si-MCM-41 synthesized following a reported methodology [31], as follows: a suspension of 10 g Si-MCM-41 in 250 mL dry CCl_4 was refluxed for 1.5 h, while bubbling moisture-free N_2 (30 mL/min) through the mixture. Then 2.6 g (19 mmol) of anhydrous $AlCl_3$ were added, and the resulting mixture was refluxed under the N_2 flow for another 3 h. The obtained $AlCl_3$/MCM-41 suspension was filtered out, washed with CCl_4 and dried under vacuum at 353 K. The resulted sample was characterized by a series of techniques such as nitrogen adsorption–desorption isotherms at 77 K, XRD, XPS, TEM, and FT-IR. Detailed procedures were given elsewhere [31]. The commercial zeolites have been characterized as well using nitrogen adsorption–desorption isotherms, NH_3-TPD, Py-FT-IR and dynamic light scattering experiments (DLS). The surface areas were estimated according to the BET model from *ex situ* BET nitrogen physisorption isotherms at 77 K that were recorded on a Micromeritics ASAP-2010 automated instrument. Calcined samples were degassed for 15 h at 403 K and 10^{-6} Torr before analysis. The NH_3-TPD profiles were obtained using a Micromeritics AutoChemII apparatus equipped with a programmable temperature furnace and TCD detector. 0.5 g of sample was purged for 2 h with 40 mL/min He at 773 K, after the increase of temperature from ambient to 773 K using a heating rate of 5 K/min, followed by lowering temperature to 353 K. Then, 3% NH_3/He was flushed for 30 min at 353 K, and then purged with 40 mL/min He at 373 K for 1 h. After that, under the same flow of He, the temperature was raised from 373 K to 873 K at 10 K/min, analyzing the desorbed ammonia. The weak, medium, and strong acidities were assigned to the peaks of NH_3-TPD profiles lower than 623 K, between 623 and 773 K, and above 773 K, respectively. FT-IR measurements were performed at room temperature on a Magna-IR 550 FTIR spectrometer from Nicolet, using a MCT-B liquid nitrogen cooled detector, and equipped with a heatable cell (up to 773 K) with NaCl windows connected to a vacuum system and a gas manifold. Samples in the form of self-supporting pellets (around 5 mg/cm^2) were placed into a carousel sample holder for up to 6 pellets. Usually 200 scans were recorded at a resolution of 2 cm^{-1} for a single spectrum. FTIR spectra were normalized to the weight of 10 mg/cm^2. Prior to adsorption of pyridine (Py) the samples were dehydrated by evacuation at 673 K, overnight. The FTIR spectra were recorded after desorption of pyridine at RT, 423, 523, 623 and 723 K, respectively. All measured spectra were recalculated to a 'normalized' wafer of 10 mg. For a quantitative characterization of acid sites the following bands and absorption coefficients were used: pyridine PyH^+ band at 1545 cm^{-1}, ε = 0.078 cm µmol^{-1}, pyridine PyL band at 1454 cm^{-1}, ε = 0.165 cm µmol^{-1} [32].

Particle size distribution was determined from DLS measurements using a Mastersize2000 from Malvern Instruments.

The benzylation reactions were carried out in free solvent conditions in magnetically stirred 20 mL glass reactors (methodologies A and B) and in continuous flow conditions (methodology C). In a typical procedure, the catalyst (0.12–0.60 g) was mixed with 3.56 mL (40 mmol) of benzene and 4.16 mL (40 mmol) of benzyl alcohol. All reactions were carried out at 323–423 K for 5 min-6 h under vigorous stirring (1400 rpm). Each reaction was carried out following three methodologies: (A) by adding all benzyl alcohol at the

Table 1
Textural properties of the investigated catalysts.

Zeolite	Surface area (m^2/g)	Pore volume (mL/g)
HSZ 600	438	0.18
CBV 20A	362	0.16
PQ25	465	0.19
PQ75	534	0.18

beginning of the reaction, (B) by dropwise addition of benzyl alcohol (1–2 drops/min for 4 h) and (C) flow conditions (with different: molar ratio of B/BnOH: 1/1, 5/1, 10/1; flow: 0.1, 0.2 and 0.3 mL/min and temperature: 373 K and 423 K). After the reaction was stopped (methodologies A and B), the catalyst was filtered off and the reaction product was analyzed through GC (Shimadzu instrument with FID detection, TR-WAX-TR1MS column of 60 m length and 0.32 mm inner) and characterized by GC–MS (TERMO Electron Corporation instrument).

The reactivation of the catalysts was carried out following a procedure described elsewhere [33,34]. The catalysts were calcined with 5 K min^{-1} till 373 K, and then with 1 K min^{-1} till 773 K, where they were kept for 4 h.

3. Results and discussion

3.1. Catalysts characterization

Table 1 shows the textural properties of the investigated zeolites. While some differences were observed among the surface areas, depending both on the Si/Al ratios and the type of zeolite, the pore volume of these materials is very close, that is in a very good concordance with the typical high external surface area of beta zeolites.

From structural point of view, there are some differences among the two classes of zeolites (e.g., mordenites and beta zeolites): while beta zeolite has a three-dimensional channel system with 12-membered ring channels (0.76 nm × 0.64 nm), mordenites are characterized by a bi-dimensional channel system with straight 12-membered ring channels (0.65 nm × 0.70 nm) with crossed 8-membered ring channels (0.28 nm × 0.57 nm) [35].

The total acidity of zeolites was investigated by NH_3-TPD while the pyridine adsorption gave information about the acidity type and strength (Brønsted and/or Lewis).

Fig. 1 shows the NH_3-TPD profiles of the above zeolites. Mordenites showed two large peaks one below 473 K assigned to weak acid sites and another at 773–873 K assigned to strong acid sites. The physical assignment of the low temperature peak received in the literature different assignments: chemisorption of NH_3 to zeolite cations, to weakly acid silanol groups or to weak Lewis acid sites [36–39]. Contrarily to mordenites the NH_3-TPD profiles of beta zeolites corresponded to only one peak centered very close to 700 K and assigned to a medium-to-strong acidity. However, the peaks of both mordenite and beta show a quite large non-symmetry that can be interpreted in the sense they correspond to the contribution of several surface species with similar acid strength.

According to Camilot et al. [40], in the case of beta zeolites, the non-symmetry is explained by two maxima: a first one, more intense, at about 683 K and another at 702 K. As the aluminum content decreased the intensity of the peak at 683 K diminishes faster than the second one and this latter is shifted about 17 K to higher temperatures. The shift of the second peak indicates an increase in acid strength of the sites that according to these authors [40] can be attributed to a higher proton activity as a consequence of the lower negative charge density of the zeolite framework. A similar effect can be expected to mordenites as well.

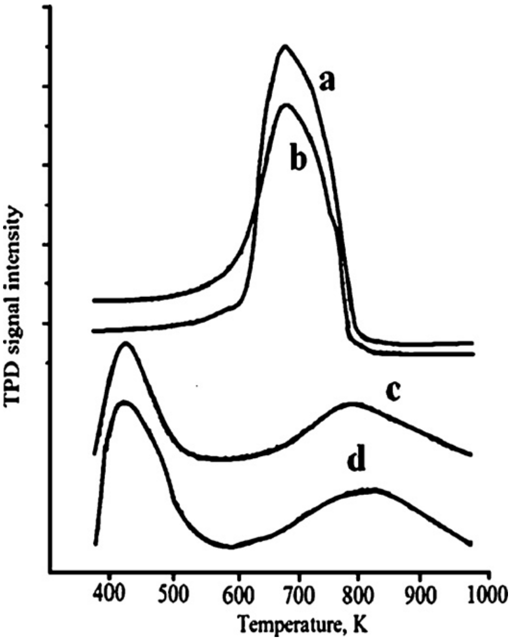


Fig. 1. NH_3-TPD profiles of the investigated zeolites: (a) PQ 25; (b) PQ 75; (c) CBV 20A; (d) HSZ 600.

The percent of the medium-to-strong acid sites from the total number of acid sites was about 49% for PQ 25, 43% for PQ 75, 39% for CBV 20A, and 34% for HSZ 600, respectively.

Py-FTIR spectra revealed the presence of Lewis acid sites as characterized by the 8a adsorption mode of Py (band at 1620 cm^{-1}) and the presence of Brønsted acid sites as characterized by the 8a adsorption mode of Py (band at 1638 cm^{-1}). The other bands in these spectra correspond to the 19b adsorption mode of Py (1445 and 1545 cm^{-1}), characteristics to Lewis and Brønsted acid sites, respectively, while those at 1490 and 1595 cm^{-1} are characteristics to pyridine physically adsorbed. The band at 1490 cm^{-1} may contain a contribution of PyP (Van der Waals interaction) and PyH (H-bond interaction) species but also of PyL (interaction with Lewis sites) and PyB (interaction with Brønsted sites) species [41]. The kinetic diameter of pyridine (0.5 nm) allows it to react with all acidic hydroxyl groups located in the 12-ring channels (0.76 nm × 0.64 nm) of beta zeolites but in the case of mordenites, hydroxyl groups located in 8-ring channels (0.26 nm × 0.57 nm) are inaccessible for steric reasons. Nevertheless, these sites are not accessible for reactants as well. In agreement with Čejka et al. [42] the acidity measured in this manner is more adequate to the actual catalytic capability of these zeolites.

In Fig. 2 are exemplified Py-FTIR spectra at different Py-desorption temperatures on PQ25 beta zeolite sample. During desorption, the band of PyH^+ species (1545 cm^{-1}) systematically decreases while a new band located at 1462 cm^{-1} start to appear [43]. The latter band (assigned to iminium ions, formed by the attack of protons on the pyridine complex bonded to Lewis acid sites: $C_5H_5NL + H^+ = C_5H_5NL^+$ [42]) increases with desorption temperature, which can be due to the combined effect of pyridine migration and "in situ" formation of stronger Lewis sites. The intensity of the iminium ion band relative to that of PyL (1462 and 1450 cm^{-1}) increased distinctly with the increase of the desorption temperature. The increase of the desorption temperature generates the removal of Py from both Brønsted and Lewis sites and causes an increased distance between these sites, and also of the average acid strength of the remaining hydroxyl groups (and hence the mobility of the protons). This is most likely the reason for

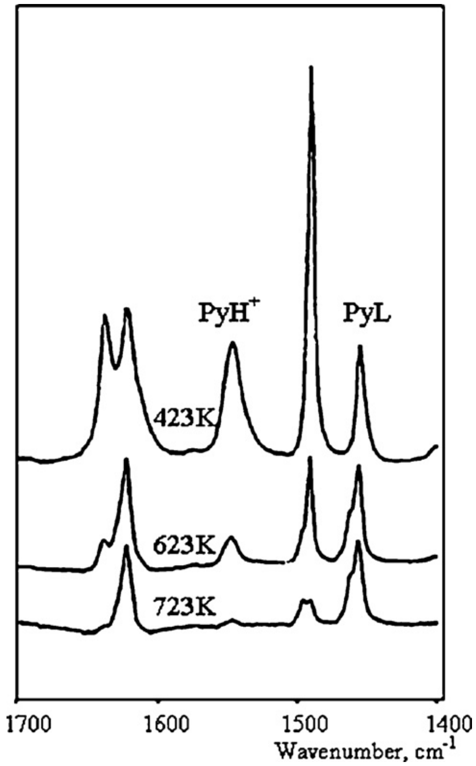


Fig. 2. Py-FTIR spectra at different Py-desorption temperatures on PQ25 beta zeolite sample.

the increase of the number of iminium ions formed per PyL [44]. In accordance with Čejka et al. [45] two processes could operate simultaneously at 723 K: pyridine desorption and dehydroxylation of liberated OH groups. As some part of the hydroxyl groups is still kept by pyridine, dehydroxylation is somehow restricted, as not enough OH groups are available for further condensation.

It is worth to note that for most of the zeolites, Lewis acid sites are much stronger than the Brønsted acid sites. The Py-desorption spectra (Fig. 2) confirm this fact, at 723 K the amount of strength Lewis acid sites being by far higher than the strength Brønsted acid sites. Table 2 gives the relative population of these sites and their concentration.

3.2. Benzylation of benzene following the methodology A

Table 3 depicts the results of benzylation of benzene with benzyl alcohol (BnOH) as alkylating agent over the investigated zeolites H-beta (PQ25 and PQ75) and mordenite (CBV 20A and HSZ 600) (Scheme 1). Obviously, the benzyl alcohol is a less reactive alkylating agent than benzyl chloride, and as a result, it is expectable a reaction rate to diphenylmethane (DPM) inferior to those reported with benzyl chloride [11]. Under the investigated conditions H-beta zeolites were more active compared to mordenites (entries 1–2 versus entries 3–4). In terms of selectivity, H-beta zeolites were also found to be more selective than mordenites in this reaction although the selectivity is not satisfactory. Both the activity and selectivity were affected by the Si/Al molar ratio for both zeolites (Beta and Mordenite). A higher Si/Al molar ratio was found to allow an increased BnOH conversion. For example, after 2 h, the conversion of BnOH on PQ75 sample (H-beta zeolite; Si/Al = 35.8) was almost 66%. The results are in contradiction with early reports [11] showing that a high Si/Al molar ratio of H-beta lowers the alkylating agent (benzyl chloride) conversion.

It is well known that a higher Si/Al ratio decreases the density of acid sites and increases their strength. To generate the electrophile ($C_6H_5CH_2^+$) needed for the Friedel-Crafts alkylation, the benzyl alcohol requires stronger acid sites. Furthermore, it was observed for both zeolites that the selectivity to DPM is significantly affected by the Si/Al ratio, especially in the case of mordenite zeolites. Thus, apart the high DBE formed amounts, high molecular weight polybenzylated by-products were also observed, their concentration depending on the type of catalyst. The lower selectivity to DPM at higher Si/Al ratios can be attributed to the residual Brønsted acid sites, which seems to be also the main responsible for catalyzing the consecutive reactions in the benzylation of benzene. However, the variation of the BnOH conversion and the selectivity to DPM do not parallel the Si/Al molar ratio (Table 3, entries 2 and 3) showing that the zeolites behavior is dictated not only by their acidity but also by their porosity. Accordingly, although the difference in the Si/Al molar ratio for PQ25 Beta zeolites (Si/Al = 10.8) and CBV 20A mordenite (Si/Al = 10.0) is insignificantly large differences were observed in the case of selectivity to DPM (it decreased from 30.9% for PQ25 Beta to 3.1% for CBV 20A mordenite), while the observed difference in the conversion of BnOH is quite low (48.4% in the case of PQ25 Beta versus 44.5% in the case of CBV 20A mordenite). A somehow surprising result was obtained on HSZ 600 mordenite (Table 3, entry 4), in the presence of which the amount

Table 2
The relative population of the Brønsted and Lewis acid sites and the concentration of Brønsted and Lewis sites.

Zeolite	Si/Al molar ratio	Brønsted acid site[a]	PyH^+ mmol/g[b]	Lewis acid site[a]	PyL mmol/g[b]
PQ 75	35.8	0.21	0.016	0.051	0.008
PQ25	10.8	0.9	0.07	0.7	0.11
CBV 20A	10.0	0.415	0.03	1.56	0.26
HSZ 600	3.0	0.605	0.047	2.64	0.43

[a] Calculated by the ratio of the integrated area of IR adsorption peak to sample weight (Py desorption – 423 K).
[b] Calculated from the absorption coefficients [32].

Table 3
Benzylation of benzene with benzyl alcohol catalyzed by zeolites following methodology A.

Entry	Catalyst	Si/Al molar ratio	C_{BnOH} (%)	S_{DPM} (%)	By-products (%)	
					DBE	Polyalkylated benzenes
1	PQ75	35.8	65.8	21.7	71.6	6.7
2	PQ25	10.8	48.4	30.9	63.5	5.6
3	CBV 20A	10.0	44.5	3.1	94.0	2.9
4	HSZ 600	3.0	38.9	9.1	73.3	17.6

Reaction conditions: 3.56 mL (40 mmol) of benzene; 4.16 mL (40 mmol) of BnOH; 600 mg of catalyst; reaction temperature = 353 K; reaction time = 2 h.

of polyalkylated benzene by-product was considerably higher than on the other catalysts. Such a behavior proves once more the effect of both the chemical and textural zeolite characteristics upon the catalytic performances.

Increasing the reaction temperature to 373 K, as expected, was leading to an increase of the conversion of BnOH, irrespective of the zeolite nature, but the selectivity was still far on those of practical interest (Table 4). However, although the change in the temperature was small a different change in the selectivity has been observed as a function of the zeolite nature. Thus, in the case of Beta zeolites (Table 4, entries 1 and 2), the increase of the temperature lowers the selectivity to DPM while for mordenites, the same increase of temperature led to a higher selectivity in DPM (Table 4, entries 3 and 4).

At higher temperatures and in the presence of Beta zeolites, the decrease in the selectivity to DPM may be attributed to the formation of higher amounts of by-products (e.g., DBE and polyalkylated benzene). In the case of mordenites, the different porosities connected with a certain surface chemical composition changes again the product distribution.

To the same temperature (373 K) and a longer reaction time (4 h) the selectivity to DPM is slightly increased (Table 5). Moreover, the amount of the catalyst used in the reaction influence both the conversion of BnOH and the selectivity to DPM. In Table 5 are presented the results obtained using different amounts of PQ25 Beta zeolite (0.03–0.15 g). Nevertheless, for the same amount of catalyst (0.15 g) the selectivity to DPM is slightly lower at 373 K after 4 h (Table 5, entry 6) than at 353 K after 2 h (Table 3, entry 2) but slightly higher than at 373 K after 2 h (Table 4, entry 2).In conclusion, following the methodology A the etherification of benzyl alcohol to DBE is faster than the benzylation of benzene DPM [45]. On the other hand, the variation of the selectivity to DPM as a function of the reaction temperature and time suggest that the generated dibenzyl ether (DBE) acts as an alkylating agent.

3.3. Benzylation of benzene following the methodology B

A common procedure to favor the increase of the conversion is to work in an excess of the substrate. Nevertheless, such an approach comes in contradiction with the principles of green chemistry, any excess of the reactants assuming not only higher raw materials consumption but also the generation of wastes. Having these in mind, experiments in which BnOH was dropwise added finally reaching a molar ratio of the reactants of 1/1 have also been carried out. In this way it is generated an apparently high excess of one of the substrates into the reaction medium and the etherification reaction may be confined.

Table 6 presents the reaction results following the methodology B, at 353 K. Tested zeolites were compared with two other catalytic samples with strong pure Brønsted acidity (SAC-13; Nafion (13 wt%) embedded silica; amount of acid sites: 0.15 mequiv./g, $H_0 \geq -12$; $D_p = 10$ nm) or pure Lewis acidity ($AlCl_3$/MCM-41, amount of active phase = 1.9 mmol/g; $D_p = 2.4$ nm)). As Table 4 shows, the major improvement is that in the presence of zeolites, the dropwise addition of BnOH improves the selectivity to DPM in high degree, thus approaching values of practical interest. Using PQ75 zeolite, following this procedure the selectivity in DPM was of 65% for a conversion of 62% in 4 h, and with PQ25 the selectivity in DPM was 77% for a conversion of 58% under the same experimental conditions. An improvement was observed in fact for all zeolites. Keeping the system for another 2 h under the same experimental conditions was not accompanied by significant changes. Noteworthy, the behavior of zeolites beta was superior to that of SAC-13 or of $AlCl_3$/MCM-41 catalysts.

These data suggest that in fact the benzyl alcohol activation does not require a very strong acidity, and a middle-strong acidity as it is that characteristic to beta zeolites is sufficient to generate electrophile ($C_6H_5CH_2^+$) species necessary for Friedel-Craft alkylation. Moreover, higher acidity strength (e.g., SAC-13 sample) favors the etherification thus decreasing the selectivity to the alkylated product, while the low activity $-OAlCl_2$ and $-O_2AlCl$ units formed during the immobilization of $AlCl_3$ on the surface of MCM-41 sample [31] led to a decrease of both the conversion of benzyl alcohol and the selectivity to DPM. Therefore, the nature of the catalyst has a considerable influence on the reactivity and selectivity of the alkylating agent, the activated electrophile species existing as a more or less tight ion pair with a considerable degree of covalent bonding between the carbocation and the catalyst macroanion. In these conditions, its relative stability is very important for determining the rate of alkylation.

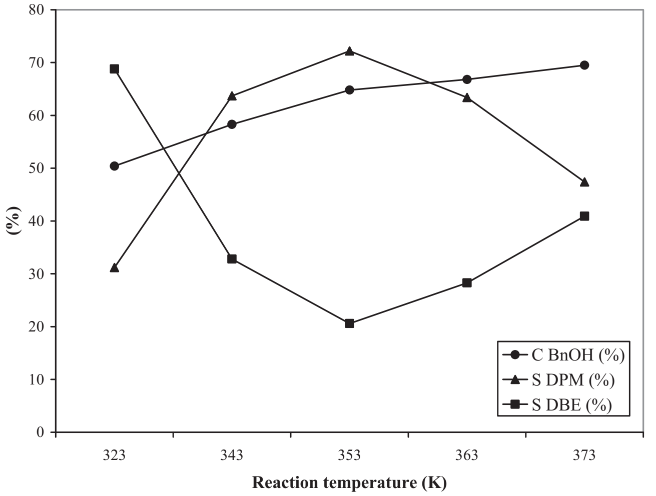


Fig. 3. The variation of the conversion of BnOH and selectivities to DPM and DBE as a function of the reaction temperature following methodology B (reaction conditions: reaction mixture: substrate = 3.56 mL (40 mmol); BnOH = 4.16 mL (40 mmol); amount of PQ25 catalyst = 600 mg; reaction time = 2 h).

In addition, pores in the domain of mesopores, as in the case of SAC-13 and $AlCl_3$/MCM-41, allow the formation of by-products such as polyalkylated benzenes and DBE, thus decreasing the selectivity to the main reaction product – DPM.

The dependence of the conversion and the selectivity to DPM on the reaction temperature was investigated using PQ25 Beta zeolite, in a range of 323–373 K (Fig. 3).

As we expected the conversion of BnOH was found to increase with the increase of the reaction temperature. However, like in the experiments carried out following the methodology A, the selectivity to DPM registered a maximum value (72.2%) at 353 K. At higher temperatures (373 K), the decrease in DPM selectivity is attributed to the formation of bulkier polybenzylated as consecutive products and to the etherification to DBE.

3.4. Benzylation of benzene following the methodology C

The use of flow methodology brings several technical advantages as, for example, the improved heat and mass transfer and the precise control over reaction conditions. Such technical advantages bring in turn important improvements of the chemical reaction in terms of yield improvement, better selectivity and reproducibility.

An optimization of the benzylation can be made by varying different reaction parameters as: temperature (373–423 K), flow rate of the reactants (0.1–0.3 mL/min), and benzene/BnOH molar ratios (1/1–1/10). The most significant results are presented in Tables 7 and 8. As Table 7 shows, in the presence of PQ25 beta zeolite and flow rate of 0.2 ml/min, the conversion of BnOH increases from

Table 4
Benzylation of benzene with benzyl alcohol at 373 K following methodology A.

Entry	Catalyst	Si/Al molar ratio	C_{BnOH} (%)	S_{DPM} (%)	By-products (%)	
					DBE	Polyalkylated benzenes
1	PQ75	35.8	72.1	15.6	77.8	6.6
2	PQ25	10.8	72.6	18.7	77.9	3.4
3	CBV 20A	10.0	45.9	16.3	80.7	3.0
4	HSZ 600	3.0	51.8	30.9	57.8	11.3

Reaction conditions: 3.56 mL (40 mmol) of benzene; 4.16 mL (40 mmol) of BnOH; 600 mg of catalyst; reaction temperature = 373 K; reaction time = 2 h.

Table 5
Benzylation of benzene with benzyl alcohol with different amounts of PQ25 Beta zeolite following methodology A.

Entry	PQ25 beta catalyst (mg)	C_{BnOH} (%)	S_{DPM} (%)	By-products (%)	
				DBE	Polyalkylated benzene
1	120	63.2	17.7	75.9	6.4
2	200	67.8	19.1	74.5	6.4
3	300	76.2	19.9	74.0	6.1
4	400	72.3	21.9	73.2	4.9
5	500	80.3	22.5	72.7	4.8
6	600	83.5	25.6	69.8	4.6

Reaction conditions: 3.56 mL (40 mmol) of benzene; 4.16 mL (40 mmol) of BnOH; temperature = 373 K; reaction time = 4 h.

Table 6
The benzylation of benzene following methodology B.

Entry	Catalyst	C_{BnOH} (%)		S_{DPM} (%)		By-products (%)			
						DBE		Polyalkylated benzenes	
		4 h	6 h	4 h	6 h	4 h	6 h	4 h	6 h
1	PQ75	62.4	64.2	65.5	63.2	27.8	31.3	6.7	5.5
2	PQ25	57.9	64.8	77.0	72.2	17.2	20.6	5.8	7.2
3	CBV 20A	41.2	42.1	29.2	29.1	70.8	70.9	0	0
4	HSZ 600	43.5	44.7	42.9	42.3	56.3	56.7	0.8	1.0
5	SAC-13	59.9	61.4	21.0	16.2	71.6	77.7	7.4	6.1
6	$AlCl_3$/MCM-41	37.0	41.9	3.1	3.3	91.9	83.9	5.0	12.8

Reaction conditions: reaction mixture: 3.56 mL (40 mmol) of benzene; 4.16 mL (40 mmol) of BnOH; 600 mg of catalyst; reaction temperature = 353 K; reaction time = 4 h and 6 h, respectively (including the dropwise adding time of BnOH).

Table 7
Benzylation of benzene with benzyl alcohol at 373 K following methodology C.

Entry	Molar ratio-B/BnOH	C_{BnOH} (%)	S_{DPM} (%)	By-products (%)	
				DBE	Polyalkylated benzene
1	1/1	20	24.8	75.2	1.7
2	5/1	89.8	50.1	49.9	1.8
3	10/1	99.2	88.9	9.4	1.7
4*	10/1	96.8	56.7	43.3	0.2

Reaction conditions: 3.56–35.6 mL of benzene; 4.16 mL of BnOH; 600 mg of catalyst PQ25; temperature = 373 K; and *methodology A: 35.6 mL of benzene; 4.16 mL of BnOH; 600 mg of catalyst; temperature = 373 K, reaction time = 2 h.

Table 8
Benzylation of benzene with benzyl alcohol at 423 K following methodology C.

Entry	Molar ratio-B/BnOH	C_{BnOH} (%)	S_{DPM} (%)	By-products (%)	
				DBE	Polyalkylated benzene
1	1/1	42.7	3.3	96	0.7
2	5/1	97.1	34.7	64.5	0.8
3	10/1	96.4	76.7	23	0.3

Reaction conditions: 3.56–35.6 mL of benzene; 4.16 mL of BnOH; 600 mg of catalyst PQ25; reaction temperature = 423 K.

20% to 99.2% with the increases of the benzene/BnOH molar ratio from 1/1 to 10/1 (entries 1–3). The selectivity to DPM paralleled the conversion of BnOH increasing from 24.8 to 88.9%.

For a more realistic evaluation of the reactor-catalyst efficiency, both reactants (e.g., benzene and benzyl alcohol) were flowing continuously through the reactor until the efficiency of the process decreased. The reaction products were analyzed every 10 min (Fig. 4).

As Fig. 4 shows, after approximately 2 h the conversion of BnOH started to decrease, indicating that the active sites become

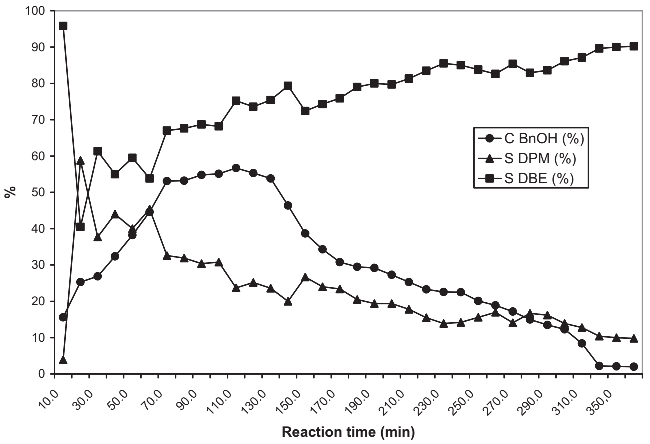


Fig. 4. Benzylation of benzene with benzyl alcohol at 373 K following route C (reaction conditions: B/BnOH molar ratio = 10/1: 35.6 mL of benzene and 4.16 mL of BnOH; 600 mg of catalyst PQ25; temperature = 373 K; flow rate of the reactants = 0.2 mL/min; time = 10 min for each reaction).

progressively poisoned by the polyalkylated benzenes formed as by-products (<2%; not shown in Fig. 4). After cca. 7 h the catalyst was almost completely deactivated and the conversion of BnOH was 2.2%.

Interestingly, after the first 10 min, the selectivity to DPB was only 3.9% while the selectivity to DBE was of 95.8%, after 10 min the selectivity of DBE decreased at 40.5% while the selectivity of DPB increased at 58.8%. The increase of the conversion of BnOH from 15.6% after the first 10 min to 25.3% after 20 min does not justify the high difference in the DPM selectivity (from 3.9% to 58.8% in this reaction period). To explain these results we have to take into consideration that the benzylation takes place through a mechanism which involves as benzylation agents both BnOH and DBE, in agreement with data reported previously [46] (Scheme 2).

Keeping the same reaction conditions but changing the reaction methodology (from C to A) the selectivity to DPM was drastically reduced while the conversion of BnOH remained at the same level (Table 7, entries 3 and 4).

As for the other cases, the increase of the reaction temperature led to an increase of the conversion of BnOH while the selectivity to DPM showed a major decrease (Table 8) in the favor of the DBE and polyalkylated benzene.

Irrespective of the experimental methodology (Tables 3–8) the zeolite PQ25 was the most effective catalyst. Actually, the performances of the catalysts followed the order PQ25 > PQ75 > HSZ600 > CBV20A. This order paralleled perfectly the order of the particle size 34.3 μm (PQ25) > 28.7 μm (PQ75) > 6.4 μm (HSZ600) > 3.8 μm (CBV20A) (Fig. 5).

The performances of the catalysts also follows fairly good the percent of the medium-to-strong acid sites from the total number of acid sites PQ 25 (49%) > PQ 75 (43%) > CBV 20A (39%) > HSZ 600 (34%). Exception makes only CBV 20A and HSZ 600 but for the last one the particle size is larger.

However, no alteration of the kinetics as an effect of the internal diffusion linitation has been evidenced. The calculation of the Thiele modulus modified by Weisz [47–49]

$$\varphi = \frac{\nu R^2}{D_{\text{eff}} C_0}$$

where ν is the rate (mol s g^{-1}) calculated for conversions smaller than 15%, R is the radius of the catalyst grains, C_0 is the concentration (mol ml^{-1}), and D_{eff} is the diffusion coefficient (cm^2 s^{-1}) indicated that indeed the diffusion resistance is absent, and the reaction rate is representative of activity for the comparison of different catalysts. These values are much smaller than 1, i.e. the value for which is accepted the diffusion limits the overall process (Table 9). In addition the differences between the values measured for the two supports are in concordance with the larger pore sizes of the beta-zeolites. However, there are strong arguments the reaction occurs on the external surface of the catalysts that is quite contradictory with these results.

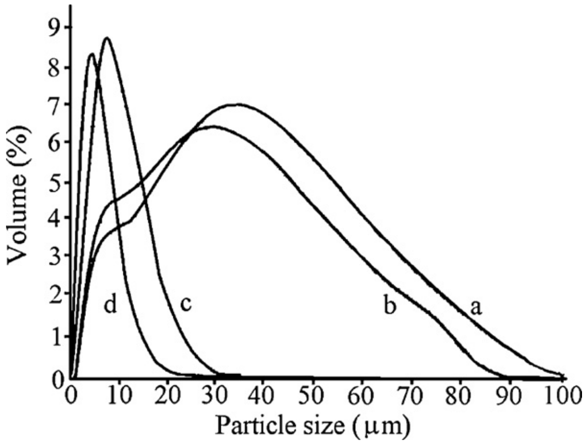


Fig. 5. Particle size distribution of zeolite catalysts: (a) PQ 25 (*d* = 20. A 8.9 (sh), and 34.3 μm); (b) PQ 75 (*d* = 8.7 (sh), and 28.7 μm); (c) HSZ 600 (*d* = 6.4 μm); (d) CBV 20A (*d* = 3.8 μm).

Table 9
Thiele modulus modified by Weisz for the investigated catalysts.

Zeolite	PQ 75	PQ25	CBV 20A	HSZ 600
φ	9.13×10^{-2}	9.56×10^{-2}	0.001×10^{-2}	0.003×10^{-2}

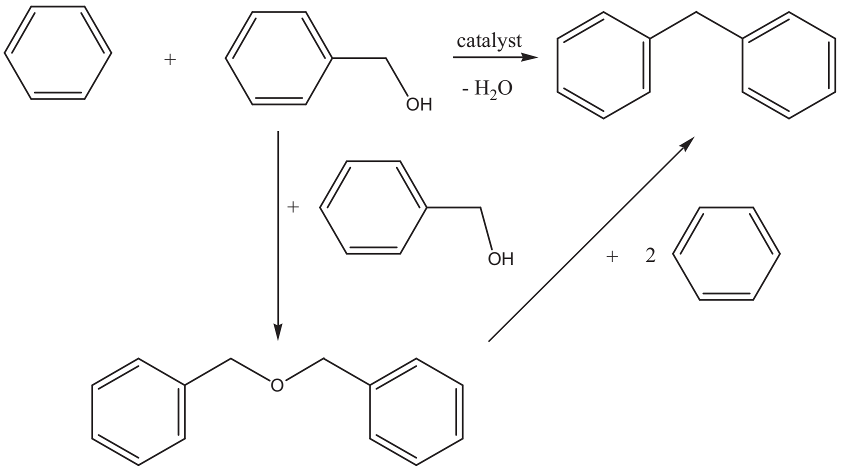
Subtle differences between zeolites of similar pore sizes and dimensionality can be usually explained based on the differences in the acidity of the individual zeolites [42]. In the studied benzylation reaction the zeolites behavior may account for the fact the reaction occurs mainly on the external surface of the above zeolites. However an analysis of the selectivities in this case is speculative and has little sense since most of the acid sites are distributed within the grain and only those situated at the surface work.

These data also show that the behavior is different working with benzyl alcohol instead of benzyl chloride. Using benzyl chloride medium-to-strong acid sites are not required maybe because of the participation of the released HCl [50]. This behavior is different using benzyl alcohol and is also confirmed by the data presented in Fig. 3 for the first 2 h reactions. The strong acid sites are necessary to generate DBE that becomes the alkylating agent. Once, these sites are blocked further reaction of DBE is limited and both the conversion and the selectivity to DPM dramatically decreased.

3.5. Recycle experiments

PQ75 Beta zeolite used in the benzylation of benzene was recycled four times in order to check the activity, stability and reusability of the catalyst following the methodology A. After completion the reaction on fresh catalyst, the catalyst was separated from the reaction mixture by filtration, washed with acetone and calcined at 773 K for 4 h in the presence of air. The PQ75 catalyst practically kept the activity and selectivity to DPM after each cycle (Table 10) irrespective of the reaction methodology has been used.

This is another important advantage of using BnOH since studies using benzyl chloride as alkylating agent reported a loss of the activity after recycling, although in a low extent, due to a minor



Scheme 2. Friedel-Crafts benzylation of benzene involving both BnOH and DBE as benzylation agents.

Table 10
Recycling of PQ75 zeolite in four catalytic runs.

Entry	Run	C_{BnOH} (%)	S_{DPM} (%)
1	Fresh catalyst (1st run)	65.8	21.7
2	2nd run	65.6	21.3
3	3th run	65.7	21.4
4	4th run	65.6	21.5

Reaction conditions: 3.56 mL (40 mmol) of benzene; 4.16 mL (40 mmol) of BnOH; 600 mg of catalyst; reaction temperature = 353 K; reaction time = 2 h.

dealumination of the zeolite by HCl, which is produced during the reaction as a byproduct [11,51,52].

Using benzyl alcohol as alkylating agent the only inorganic by-product formed during the reaction is water. However, it seems that even the formed water blocks the acid sites and the prolongation of the reaction time is leading to a plateau in the benzyl alcohol conversion (Table 6). A simple azeotropic removal of water during the reaction may solve this inconvenient.

4. Conclusion

This catalytic study demonstrated that the benzylation of benzene can be carried out in "green" advantageous conditions even by using a less reactive alkylating agent as benzyl alcohol and catalysts with strong acidity as Beta zeolites. The conversion and product distribution largely depends on the experimental conditions and the zeolite nature. Under optimal conditions following the dropwise reactant addition methodology, selectivities of 77% in DPM were achieved for conversion of BnOH of 58% in 4 h of reaction at 353 K. Under these conditions, stronger acid catalysts as Nafion-embedded silica favor both the etherification reaction and the formation of polybenzylated products, lowering the selectivity to DPM. Also, the conversion of BnOH remained in the range of the values obtained with zeolites.

Recycling tests showed that the catalysts kept the activity and selectivity to DPM at least for four reaction cycles. In conclusion, the use of benzyl alcohol instead of benzyl chloride as alkylating agent offers not only the advantage of avoiding the formation of toxic wastes as inorganic by-products but also preserves the initial catalyst activity.

The described flow procedure (methodology C) has high advantages over all known processes for the synthesis of diphenylmethane (DPM). Therefore, at optimum reaction conditions a selectivity of almost 90% of DPM, for a conversion of 99.2% of BnOH can be obtained.

It has to be pointed out that the catalytic system has also some practical advantages such as: (i) availability and low costs of the catalysts; (ii) simple and practical experimental set-up; (iii) easier purification of the final product due to the lower content of by-products. The catalytic efficiency combined with practical advantages of the catalytic experimental set-up and the "green" elements of the reaction itself make this process appealing even in the commercial stage.

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