

## Replacing benzyl chloride with benzyl alcohol in heterogeneous catalytic benzylation of aromatic compounds\*

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**Abstract:** Comparative catalytic liquid-phase benzylation of aromatic compounds (e.g., benzene and ethylbenzene) to diphenylmethane (DPM) derivatives with benzyl alcohol (BnOH) was investigated over various catalysts like zeolite (HSZ 600 mordenite, CBV 20A mordenite, H-beta zeolites with Si/Al ratios of 10.8 and 35.8, respectively) and nanostructured inorganic fluorides (MgF<sub>2</sub>) at 80–120 °C under atmospheric pressure. The reactions were carried out in batch reactors using two methodologies: (i) by introducing both the solution of substrate and BnOH at the beginning of the reaction, and (ii) by drop-wise addition of BnOH (1–2 drops/min for 4 h) to the reaction mixture. The analysis of the reaction products indicated that the conversion and product distribution depend on the experimental method and the nature of the catalyst. The reaction rate was found to correlate to the nucleophilicity of the substrates and their ability to delocalize the positive charge in the Wheland intermediate by inductive and resonance effects.

**Keywords:** alkylation; benzylation; benzyl alcohol; fine chemicals; heterogeneous catalysis; inorganic fluorides; zeolites.

### INTRODUCTION

Increasingly stringent environmental legislations have generated a pressing need for cleaner methods of chemical production, for instance, new methodologies that can reduce or eliminate waste generation and avoid the use of toxic and/or hazardous reagents [1]. In this context, some of the major goals are: the development of new sustainable chemical products, the increase of the process efficiency, and a simplified process work-up in order to facilitate the recovery and reuse of the catalyst or reagents, therefore minimizing waste generation.

Diphenylmethane (DPM) and its derivatives are industrially important compounds used in pharmaceutical [2] and fine chemical [3] synthesis. In the fragrance industry, DPM has been used as both a fixative and a scenting soap. DPM has also been used as an additive with synergistic effects in insecticides, as well as a plasticizer for dyes [4]. Its synthesis is traditionally performed in environmentally

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unfriendly conditions, by using homogeneous acid catalysts, such as  $\text{H}_2\text{SO}_4$ , HF,  $\text{AlCl}_3$ ,  $\text{FeCl}_3$ , or  $\text{ZnCl}_2$  [5]. The typical criticisms of homogeneous catalysis are the difficult separation and recovery of the catalytic species from the reaction medium. Drawbacks such as the disposal of spent catalyst, the corrosion or high toxicity of the used reactants and solvents are the most prominent challenges that should obey environmental legislation. In recent years, in order to overcome these challenges, synthetic organic reactions for the fine and specialty chemical industry have been carried out utilizing heterogeneous Lewis and Brønsted acid catalysts [6]. Another proposed solution consisted of depositing various Lewis acids on different catalyst supports, such as MCM-41 [7], or hydroxyapatite (HAP) [8]. Fe-, Al-, and mixed Fe, Al-pillared montmorillonites doped with 10 % of Mo, V, or Cr [9] have also been used as heterogeneous catalysts for the benzylation of benzene and its derivatives with benzyl chloride. These heterogeneous catalysts produced good yields of monoalkylated products and made the isolation of the products and reagents easier. Despite these advantages, the preparation of these catalysts is commonly tedious, and they deactivate rapidly owing to the coke formation.

Another important drawback, from a green chemistry point of view, is that benzylation reaction using chloride-based catalysts and benzyl chloride as alkylating agent generates the undesirable byproduct, hydrochloric acid (HCl). Clearly, it will be more appropriate to use benzyl alcohol (BnOH), which generates only water as the byproduct. Hence, there is still a need to develop simple and clean methodologies for the synthesis of DPM and its derivatives.

Zeolites represent one of the plausible solutions to replace the chlorine-based homogeneous catalysts. Recently, we have also developed novel nanostructured, partially hydroxylated metal fluorides with bi-acidic (Lewis/Brønsted) properties [10]. We have shown that hydroxylated nanostructured fluorides ( $\text{MgF}_2$  and  $\text{AlF}_3$ ) can be successfully applied as highly active catalysts in various syntheses [11–14]. From a green chemistry point of view, the use of fluorides is acceptable. The catalytic properties of the novel nanostructured fluoride catalysts are related to their particular structural and chemical features: (i) high surface area with pore diameters in the range of mesopores; (ii) very low solubility in strong polar solvents; (iii) hydrolysis resistance; (iv) medium-strength Lewis and Brønsted acid sites; (v) the possibility of easily tuning the surface acidity; and (vi) nanostructured particle dimension [10,15]. With the aim to extend the applicability of this promising new class of catalytically active materials, we recently applied them to the synthesis of DPM and its derivatives using a less reactive but more environmentally friendly alkylating agent, BnOH [16]. We recently demonstrated that even microporous zeolites are active and selective in the benzylation of benzene to DPM by using BnOH [17] by using an optimized reaction methodology. Under these conditions, selectivities of 77 % for DPM with a conversion of BnOH near 58 % at 353 K were achieved.

BnOH is a less reactive benzylation agent than benzyl chloride, and as a result, an inferior reaction rate to DPM [18] was expected. However, from the environmental point of view, BnOH is preferable as benzylation reagent as long as the formation of toxic wastes is avoided (e.g., HCl vs.  $\text{H}_2\text{O}$ ). But a comparable conversion rate of BnOH with that of benzyl chloride can be reached in different ways: (i) increasing the reaction temperature; (ii) using a catalyst with stronger acidity; or (iii) modifying the entire synthesis methodology.

Based on these achievements, we pursued the benzylation of benzene and ethylbenzene by using hydroxylated metal fluorides and zeolites as heterogeneous catalysts. The aim of this research was to gain deeper insight into the influence of the nature of the substrate on the reaction rate, the reaction parameters, and the reaction protocol/procedure. An optimal combination of these factors is essential to achieve an improved and greener synthesis protocol for this important reaction.

## EXPERIMENTAL

### Catalyst preparation

Commercial zeolites with different structures and chemical compositions were purchased from various companies. Large-pore mordenite (HSZ 600) with a Si/Al ratio of 3.0 was purchased from TOSOH company, mordenite CBV 20A with a Si/Al ratio of 10.0 was purchased from Zeolyst International, while two H-beta zeolites with Si/Al ratios of 10.8 (PQ25) and 35.8 (PQ75), respectively, were received from PQ-Valfor.

Nanostructured partly hydroxylated fluorides were synthesized as reported elsewhere [10] by dissolving metallic Mg (Aldrich, 99.98 %) in methanol followed by a sol-gel fluorination. All the reagents were analytically pure and were used as received from Aldrich. The prepared catalysts were referred to hereafter as  $\text{MgF}_2$ -57 and  $\text{MgF}_2$ -71 where the numbers indicate the different concentrations of aqueous HF solutions used in synthesis.

### Catalyst characterization

The commercial zeolites were characterized using nitrogen adsorption–desorption isotherms,  $\text{NH}_3$ -TPD (temperature-programmed desorption), pyroelectric-Fourier transform-infrared (Py-FT-IR), and dynamic light-scattering (DLS) experiments. Particle size distribution was determined from DLS measurements using a Mastersize2000 from Malvern Instruments; detailed procedures were given elsewhere [15]. Quantitative characterization of acidic sites was determined from FT-IR measurements with a Magna-IR 550 FT-IR spectrometer from Nicolet, the following bands and absorption coefficients were used: pyridine  $\text{PyH}^+$  band at  $1545\text{ cm}^{-1}$ ,  $\epsilon = 0.078\text{ cm} \mu\text{mol}^{-1}$ , pyridine  $\text{PyL}$  band at  $1454\text{ cm}^{-1}$ ,  $\epsilon = 0.165\text{ cm} \mu\text{mol}^{-1}$  [19].

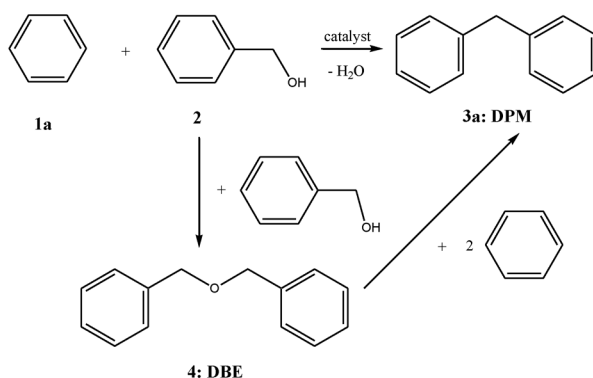
X-ray diffraction (XRD), cross polarization-magic-angle spinning-NMR (CP-MAS-NMR), transmission electron microscopy (TEM), thermal analysis, and elemental analysis were employed to study the structure, composition, and thermal behavior of the bulk fluoride materials. X-ray photoelectron spectroscopy (XPS) measurements, FT-IR with probe molecules,  $\text{NH}_3$ -TPD, and the determination of  $\text{N}_2/\text{Ar}$  adsorption–desorption isotherms were carried out to investigate the surface properties of the fluorides. All characterization procedures were described elsewhere [10,11,15,20].

### Catalytic tests

Benzylation reactions were carried out under solvent-free conditions in magnetically stirred 20-mL glass batch reactors. A typical procedure consisted of 0.12–0.60 g catalyst that was mixed with 3.56 mL (40 mmol) of benzene, or 4.80 mL (40 mmol) of ethylbenzene, and 4.16 mL (40 mmol) of BnOH (route **A**). Reactions were carried out at 323–423 K for 5 min–24 h under vigorous stirring (1400 rpm). A second route (**B**) consisted of the drop-wise addition of BnOH (1–2 drops/min for 4 h) to the reaction mixture. After the reaction was stopped, the catalyst was filtered off and the reaction product was analyzed using gas chromatography (GC) on a Shimadzu instrument with a flame ionization detector (FID), and a TR-WAX-TRIMS column of 60 m length and 0.32 mm internal diameter. Further characterization was completed by GC-MS (TERMO Electron Corporation instrument).

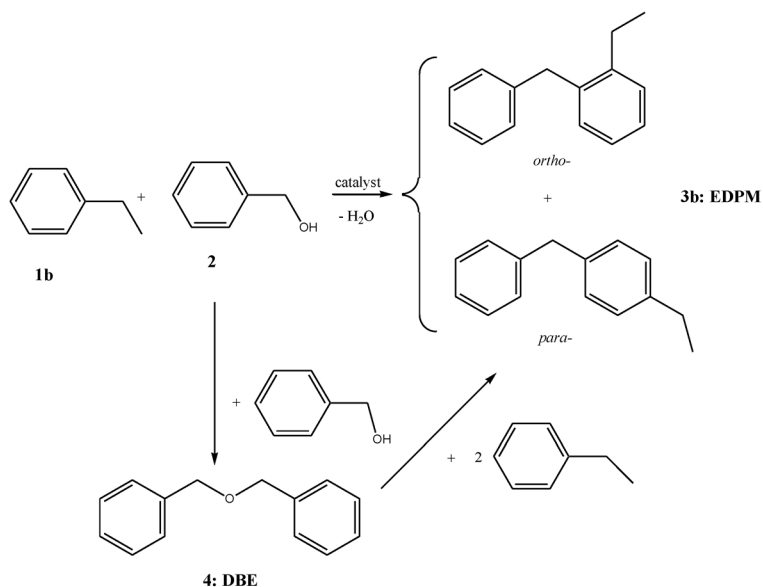
## RESULTS AND DISCUSSION

It has been established that acidic halides, which are typically Lewis acids, have little or no activity for alkylation when used as prepared. They can be activated by the addition of low concentrations of co-catalysts that interact with the Lewis acid sites to generate real or potential Brønsted sites [6]. Taking into account the chemical and textural properties of the obtained fluorides, we also applied them to the benzylation of benzene or ethylbenzene with BnOH (Schemes 1A,B).



**A. Benzylation of benzene (1a) with benzylalcohol (2)**

(DPM: diphenylmethane; DBE: dibenzyl ether)



**B. Benzylation of ethylbenzene (1b) with benzylalcohol (2)**

(EDPM: ethyldiphenylmethane; DBE: dibenzyl ether)

**Scheme 1** (A) Benzylation of benzene and (B) ethylbenzene with BnOH.

The best results obtained from the benzylation of benzene by using the route **A** are summarized in Table 1. Table 1 shows the series of hydroxylated fluorides, with the highest activity obtained from the MgF<sub>2</sub>-71 catalyst (Table 1, entries 4–6). An excess of BnOH leads to a faster transformation but, unfortunately, it predominantly results in the formation of dibenzyl ether (DBE) byproduct. With an excess of BnOH, neither the Lewis/Brønsted acid site ratio nor the acidic strength increased the selectivity to DPM. The conversion to DPM was always below 15 %, regardless of the catalyst nature or the reaction conditions.

**Table 1** The conversion of BnOH and selectivity to DPM under different reaction conditions as a function of the catalyst characteristics.

Entry	Catalyst	Si/Al ratio	T/°C molar ratio	1a/2	C/wt %	TOF/h <sup>-1</sup>	S/wt % 3a, DPM	S/wt % byproducts	
								DBE 4	Polyalkylated benzene
1	MgF <sub>2</sub> -57	–	100	1/2	11.1	1.8	3.5	96.5	0
2	MgF <sub>2</sub> -57	–	100	4/1	12.6	1.0	11.7	88.3	0
3	MgF <sub>2</sub> -57	–	120	4/1	38.2	3.1	14.5	85.5	0
4	MgF <sub>2</sub> -71	–	100	1/2	17.5	4.5	2.7	97.3	0
5	MgF <sub>2</sub> -71	–	100	4/1	18.4	2.3	10.1	89.9	0
6	MgF <sub>2</sub> -71	–	120	4/1	42.0	5.4	13.2	86.8	0
7	PQ75	35.8	80	1/1	65.8	913.9	21.7	71.6	6.7
8			100	1/1	72.1	1001.3	15.6	77.8	6.6
9	PQ25	10.8	80	1/1	48.4	89.6	30.9	63.5	5.6
10			100	1/1	72.6	134.4	18.7	77.9	3.4
11	CBV 20A	10.0	80	1/1	44.5	51.1	3.1	94.0	2.9
12			100	1/1	45.9	51.7	16.3	80.7	3.0
13	HSZ 600	3.0	80	1/1	38.9	54.4	9.1	73.3	17.6
14			100	1/1	51.8	72.4	30.9	57.8	11.3

Reaction conditions: 100 mg fluoride catalyst with 24 h reaction time; 600 mg zeolite catalyst with 2 h reaction time.

Increasing the reaction temperature is one of the options to enhance the product yield, but it contradicts one of the green chemistry principles: energy efficiency. In addition, at elevated temperatures the conversion is usually more favorable but the formation of byproducts increases. Another common procedure to favor enhancing the substrate conversion is to use an excess of one of the reagents. However, such an approach also contradicts other principles of green chemistry, atom economy, as an excess of reactants leads to not only greater raw materials consumption but also the generation of more waste. Therefore, using catalysts capable of generating higher concentrations of the electrophilic species (C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub><sup>+</sup>) from BnOH appears to be a more environmentally friendly option. If, for example, such catalysts are as widely available and inexpensive as zeolites, the process may become applicable for commercialization.

Table 1 also shows the results obtained in the benzylation of benzene in the presence of zeolites. As it can be seen that H-beta zeolites were more active and selective to DPM compared to mordenites (entries 7–10 vs. entries 11–14). For example, after 2 h at 80 °C, the conversion of BnOH on PQ75 (H-beta zeolite; Si/Al = 35.8) was almost 66 % with selectivity to DPM of almost 22 % (Table 1, entry 7). In the case of zeolites, it has been established that a higher Si/Al ratio corresponds to a decrease of the density of acid sites and an increase of the acidity strength. The results obtained in this study demonstrate that the acidic strength is one of the determining factors for conversion (e.g., higher Si/Al ratio corresponds to higher BnOH conversion). These results contradict previously reported conversions for benzyl chloride, which show a higher Si/Al molar ratio in H-beta zeolites lowers the benzylation agent conversion [18].

Both zeolites exhibited a higher selectivity to DPM compared to magnesium fluorides. However, the conversion rate was significantly affected by the variation of the Si/Al ratio. Thus, apart from the high amounts of DBE, high-molecular-weight polybenzylated byproducts were observed as well. The concentration of these species depended on the type of zeolite. The lower selectivity to DPM at higher Si/Al ratios can be attributed to the residual strong Brønsted acid sites, which are also responsible for catalyzing the consecutive benzylation of benzene to polyalkylated benzenes.

However, the variation in the selectivity to DPM is not consistent with the Si/Al molar ratio, as seen in Table 1, entries 7 and 9, which shows that the zeolites' behaviors are dictated by their porosity.

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 significant as shown by the large differences in the selectivity to DPM, decreasing from 30.9 % with PQ25 beta to 3.1 % with CBV 20A mordenite. A surprising result was seen with HSZ 600 mordenite (Table 1, entries 13 and 14), where the amounts of polyalkylated benzene byproducts were considerably higher in comparison to the other catalysts. Such a behavior exemplifies the effects of chemical and textural zeolite characteristics on their catalytic performance. Comparing the zeolite results with those obtained in the presence of nanostructured hydroxylated fluorides, it is quite clear that the increase in the BnOH conversion is attributed to the stronger acidic sites of the investigated zeolites; while the product distribution depends on both, chemical and textural characteristics. To summarize, in the presence of nanostructured fluorides after 24 h, at temperatures of 100 °C with benzene/BnOH molar ratios of 1/4, the conversions of BnOH are inferior to those obtained in the presence of zeolites. Even with only 100 mg of zeolite (e.g., PQ25) at 100 °C, similar conditions to those used in the case of the fluoride catalysts, the selectivity to DPM is 17.7 % for a conversion of BnOH of 63.5 %, after only 4 h with a benzene/BnOH molar ratio of 1/1.

The differences in chemical and textural characteristics of the two kinds of catalytic materials are significant, as adsorption–desorption isotherms of nitrogen at 77 K, and FT-IR and TPD measurements shown in Table 2 and Fig. 1. Although both kinds of materials possess Lewis and Brønsted acid sites, zeolites have stronger acidity and micropores while hydroxylated fluorides possess softer acidity and mesopores.

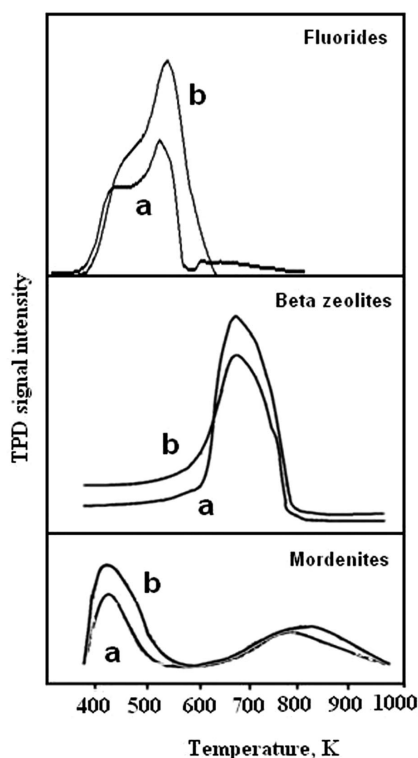
**Table 2** Textural and chemical characteristics of zeolites and hydroxylated fluorides.

Catalyst	Surface area <sup>a</sup> , m <sup>2</sup> /g	Pore volume <sup>a</sup> , mL/g	Pore size <sup>a</sup> , nm	Density of acidic sites <sup>b</sup> , mmol/g	Brønsted acid sites <sup>c</sup>	Lewis acid sites <sup>c</sup>
MgF2-57	233	0.10	2.3	0.26	1.5	1.1
MgF2-71	264	0.16	2.2	0.16	1.2	1.2
PQ75	534	0.18	<1.0	0.02	0.2	0.05
PQ25	465	0.19	<1.0	0.18	0.9	0.7
CBV 20A	362	0.16	<1.0	0.29	0.4	1.6
HSZ 600	438	0.18	<1.0	0.48	0.6	2.6

<sup>a</sup>Textural properties measured with N<sub>2</sub> at 77 K.

<sup>b</sup>Calculated from TPD measurements.

<sup>c</sup>Calculated by the ratio of the integrated area of IR adsorption peak to sample weight.



**Fig. 1** The  $\text{NH}_3$ -TPD profiles of the investigated catalysts: Mordenites: (a) CBV 20A, (b) HSZ 600; beta zeolites: (a) PQ 25, (b) PQ 75; fluorides: (a)  $\text{MgF}_2$ -71, (b)  $\text{MgF}_2$ -57.

Comparing the results obtained in the benzylation of ethylbenzene (Table 3) with those obtained in the benzylation of benzene (Table 1) with  $\text{BnOH}$  in the presence of fluorides, it is clear that the increase in turnover frequency (TOF) and, more important, the selectivity to the main product [ethyl-diphenylmethane (EDPM) vs. DPM] is a result of the substrate nucleophilicity.

**Table 3** The conversion of  $\text{BnOH}$  and selectivity to EDPM as a function of the hydroxylated fluorides and reaction conditions.

Entry	Catalyst	$T/^\circ\text{C}$	<b>1b/2</b> molar ratio	C/wt %	TOF/h <sup>-1</sup>	S/wt %		S/wt % <b>4</b> , DBE
						<b>3b</b> , EDPM <i>ortho</i>	<i>para</i>	
1	$\text{MgF}_2$ -57	100	1/2	12.8	2.0	0	4.0	96.0
2	$\text{MgF}_2$ -57	100	4/1	45.6	3.6	0.1	9.5	90.4
3	$\text{MgF}_2$ -57	120	4/1	64.0	5.1	0.2	22.3	77.5
4	$\text{MgF}_2$ -71	100	1/2	20.7	5.3	1.8	3.4	94.8
5	$\text{MgF}_2$ -71	100	4/1	51.0	6.5	4.0	7.4	88.6
6	$\text{MgF}_2$ -71	120	4/1	70.3	9.0	9.1	13.6	77.3

Reaction conditions: 100 mg catalyst, 24 h.

These results show that the electron-donating  $-\text{C}_2\text{H}_5$  group enhances the benzylation reaction because the transition state is stabilized by the electron-donating groups for both benzene and  $\text{BnOH}$ . The order of the activity of the samples was the same, the most active being the  $\text{MgF}_2$ -71 followed by

MgF<sub>2</sub>-57. The selectivity to EDPM increased by increasing the **1b/2** molar ratio as well as increasing the temperature, the highest value reaching almost 23 % at 120 °C and a **1b/2** molar ratio of 4/1.

The formation of ether observed in the described reactions was also reported for other catalysts [21–23]. Its formation was associated in all reports to Brønsted and Lewis acid sites. On the other hand, Deshpande et al. [22] reported that in the benzylation with BnOH the etherification is faster than the alkylation reaction, and the generated DBE can act as alkylating agent (see Scheme 1). Moreover, Lachter and co-workers [23] showed that the rate of the DBE formation is the same for the toluene, ethylbenzene, and propylbenzene.

An interesting feature of the benzylation of the ethylbenzene in the presence of nanostructured fluorides is the isomer composition of the reaction products. In accordance with a typical electrophilic aromatic substitution pathway, benzylation products obtained from aromatic alkylation should predominantly consist of *ortho*–*para* substituted compounds. But, in the presence of MgF<sub>2</sub>-71 catalyst ( $S_{sp} = 264 \text{ m}^2/\text{g}$ ;  $D_p = 2.2 \text{ nm}$ ; amount of acid sites = 0.16 mmol/g), the percentage of *ortho*-isomer represents 33–40 % from the total *ortho*–*para* EDPM, in the presence of MgF<sub>2</sub>-57 fluoride ( $S_{sp} = 233 \text{ m}^2/\text{g}$ ;  $D_p = 2.3 \text{ nm}$ ; amount of acid sites = 0.26 mmol/g), the main benzylation product is the *para*-isomer, with the *ortho*-isomer being formed by <1 % (see Table 3). Such behavior may be assigned to the effect of the density of the acid sites on the surface and to a lesser extent the shape-selectivity since the pore size is almost the same for both samples.

With the goal of optimizing the benzylation reactions discussed here with less reactive but more environmentally friendly BnOH, as one aspect, and the green chemistry principles, as another aspect, the next step of our research was to develop different synthesis methodologies. In this respect, experiments in which BnOH was drop-wise added until reaching a molar ratio substrate/BnOH of 1/1 have also been carried out (methodology **B**). Using this pathway in the first stage of the reaction, an excess of one of the substrates is induced.

Table 4 presents the reaction results following methodology **B**, in the presence of zeolites. The major improvement is the enhancement of selectivity to DPM that approaches values of practical applicability. Therefore, using PQ 75 zeolite and following this procedure, the selectivity to DPM was 65 % with the conversion of BnOH at 62 % in 4 h, while with PQ 25 the selectivity to DPM was 77 % with the conversion of BnOH at 58 % under the same experimental conditions. An improvement of selectivity to DPM was observed for all zeolites.

**Table 4** The benzylation of benzene in the presence of zeolites and following methodology **B**.

Entry	Catalyst	$C_{\text{BnOH}}/\text{wt } \%$	$S/\text{wt } \%$ <b>3a, DPM</b>	Byproducts/wt %	
				DBE <b>4</b>	Polyalkylated benzenes
1	PQ75	62.4	65.5	27.8	6.7
2	PQ25	57.9	77.0	17.2	5.8
3	CBV 20A	41.2	29.2	70.8	0
4	HSZ 600	43.5	42.9	56.3	0.8

Reaction conditions: reaction mixture: 3.56 mL (40 mmol) of benzene; 4.16 mL (40 mmol) of BnOH; 600 mg of catalyst; reaction temperature = 80 °C; reaction time = 4 h (including the drop-wise adding time of BnOH).

Table 5 presents the results using ethylbenzene as substrate and methodology **B**. As in the case of methodology **A** (Table 4), both the conversion of BnOH and the selectivity to EDPM are higher than in the benzylation of benzene, thus confirming that the substrate nucleophilicity is important for enhancing the benzylation reagent conversion and the selectivity to the benzylated product. However, a difference in the product distribution exists, and it consists of the fact that in the case of using zeolites the



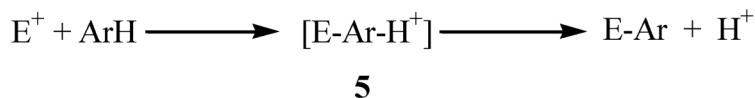
*para*-isomer of EDPM is dominant regardless of the zeolite characteristics, and less than 3 % of *ortho*-isomer is obtained. The high selectivity in *para*-isomer is strongly influenced by the zeolitic channel geometry and the transport of individual isomers into channel structure, suggesting that (i) *para*-isomer diffuses out of the zeolite pores faster; (ii) the bulky *ortho*-isomer takes a longer path to diffuse out of the molecular sieves whose spatial constraints may force isomerization to the *para*-isomer, leading to greater *para*-selectivity; and (iii) the reaction is taking place on the acid sites inside the catalyst channels.

**Table 5** The benzylation of ethylbenzene following methodology **B**.

Entry	Catalyst	C <sub>BnOH</sub> /wt %	S <sub>EDPM</sub> /wt %		Byproducts/wt %	
			<i>ortho</i>	<i>para</i>	DBE <b>4</b>	Polyalkylated benzenes
1	PQ75	71.6	2.1	73.4	20.8	3.7
2	PQ25	62.8	2.5	80.5	11.1	5.9
3	CBV 20A	53.6	1.1	38.1	60.8	0
4	HSZ600	52.5	1.4	47.5	51.1	0

Reaction conditions: reaction mixture: 4.80 mL (40 mmol) of ethylbenzene; 4.16 mL (40 mmol) of BnOH; 600 mg of catalyst; reaction temperature = 80 °C; reaction time = 4 h (including the drop-wise adding time of BnOH).

It is well known that the mechanism of alkylation initially involves the interaction of the alkylating agent with the acid catalyst to form an activated electrophile, E<sup>+</sup>, which in the second step adds to the aromatic ring acting as a nucleophile, followed by a proton loss:



where **5** is known as a Wheland intermediate [6]. The reactivity and selectivity of the alkylating agent is highly influenced by the nature of the catalyst through the relative stability of the generated active species (E<sup>+</sup>) at the catalytic active sites. Conversely, the substrate reactivity is governed by its nucleophilicity and its ability to delocalize the positive charge in the Wheland intermediate **5** by inductive and resonance effects [6]. This explains the improved reactivity of ethylbenzene over benzene.

Characterization data shows that partially hydroxylated MgF<sub>2</sub> carries Brønsted acidic OH groups instead of basic OH groups [10]. The unexpected results obtained in syntheses requiring acidity clearly indicate that the high activity in combination with an improved selectivity to the main product is due to the synergistic effect of both Brønsted and Lewis surface sites. These studies also confirmed that the best catalyst for the target product could be obtained through a very simple tuning of the acidic properties of the material [12].

## CONCLUSION

Although BnOH is less reactive than benzyl chloride, under optimized reaction conditions and in the presence of an appropriate catalyst it may constitute a greener alternative for benzylation reactions. An increase in the reaction temperature or an increase of the alkylation reagent/substrate molar ratio leads to an enhancement of both conversion of BnOH and selectivity to the benzylated product. Unfortunately, such reaction conditions contradict some green chemistry principles—energy efficiency,

atom economy, and waste generation. However, a similar level of conversion and selectivity, or even higher, could be obtained by using catalytic materials capable of generating higher concentrations of electrophilically active species ( $C_6H_5CH_2^+$ ) from BnOH. Such materials are zeolites, which are able to catalyze the benzylation of benzene with TOFs orders of magnitude greater than in the presence of fluorides. Moreover, the selectivity to benzylated product is also superior on these catalysts. Changing the substrate from benzene to ethylbenzene led to better performances that are assigned to its increased nucleophilicity.

The synthesis methodology represents another tool to improve the conversion of BnOH and the selectivity to DPM or EDPM benzylated products. It has been demonstrated that inducing an excess of the substrate in the early stage of the reaction by drop-wise addition of BnOH increases not only the conversion but also the selectivity to benzylated product. It is also worth noting that this behavior occurs at relatively low reaction temperatures and for near stoichiometric substrate/reactant ratios.

The present study offers the arguments that by choosing appropriate catalysts and synthesis methodologies, widely employed technologies using chloride-based catalysts and substrates can be replaced with more environmentally friendly ones, increasing not only the E-factor but also the conversion and selectivity.

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