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Effects of channel structures and acid properties of large-pore zeolites in the liquid-phase *tert*-butylation of phenol

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Abstract

The liquid-phase alkylation of phenol with *tert*-butanol in the presence of the H^+ form of the zeolites with FAU, BEA, and MOR topologies was investigated. Over dried catalysts, *tert*-butyl phenyl ether is the main product of alkylation. The accumulation of water molecules on the catalyst surface suppresses this reaction. The irreversible C-alkylation of phenol becomes the main reaction only after an induction period. The catalytic activity and selectivity are controlled by the porous structure and acid properties of the zeolite. The three-dimensional interconnecting pore system of Beta and USY zeolites showed a higher catalytic activity than the monodimensional system of pores of the MOR zeolites. As concerns the catalytic selectivity, the USY zeolites were selective for the *ortho*-butylation, whereas BEA zeolites were the most efficient catalysts for the *para* isomer forming.

Keywords: Phenol; *tert*-Butanol; Alkylation; Y faujasite; Beta; Mordenite

1. Introduction

Short-chain alkylphenols are important intermediates for the production of resins, antioxidants, drugs, dyes, polymer additives, agrochemicals, and antiseptic substances [1]. The direct alkylation of phenol with short-chain alcohols and olefins is widely used for the preparation of these intermediates. The catalytic reaction of phenol with *tert*-butyl alcohol or isobutene as well as with methyl-*tert*-butyl ether is an important application, because C-alkylated products such as 4-*tert*-butylphenol, 2,4-di-*tert*-butylphenol, and 2,6-di-*tert*-butylphenol have great commercial significance. Reports and patents concerning this catalytic reaction, which has been carried out both in the liquid and in the gas phase, are available [2–17]. The catalysts consist of liquid acids [2–5], metal oxides [6–9], ion-exchange resins [10–13], Al salts [14–16], and clays [17]. Some scientists recently reported the use of molecular sieves as catalysts in the butylation of phenol. Zeolites such as Y [18,19], Beta [20,21], ZSM-12, and MCM-22 [22], as well as aluminum phosphate-based molecular sieves such as SAPO-11 [23], $AlPO_4$-11, -31, -41, SAPO-11, -31, -41 [24], and AlMCM-41 mesoporous materials [25,26] were tested for this reaction.

According to these reports the molecular sieves showed high catalytic activity in the gas-phase reaction of phenol with *tert*-butanol [19–26]. The product selectivity can be controlled by the acidity of the catalyst but is less dependent on the structure of the zeolite pores. The alkylation reaction over zeolites and zeolite-like materials leads to the formation of a mixture of 2- and 4-monoalkylated products, with 4-*tert*-butyl phenol being the major product. The formation of O-alkylated phenols under these conditions has not been reported, with the exception of the study by Anand et al. [27] which states that a very small quantity of *tert*-butyl ether is formed in the presence of dealuminated HY zeolites at 100–200 °C.

In contrast, Corma et al. [18] studied the reaction of phenol with *tert*-butanol in a CCl_4 solution on HNaY zeolites; they demonstrated the presence of phenyl *tert*-butyl ether as a major product. The conversion of phenol to the corresponding ether varied from 7.6% (the total conversion of phenol is 12% mol) and 22.6% (total conversion of 30%) after 17 h of reaction. The O-alkylation was simply suppressed by a slight increase in the reaction temperature from 30 to 45 °C.

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In this study the alkylation of phenol with *tert*-butanol over acid zeolites was carried out in the slurry phase to investigate the effects of the acidity of catalysts in the absence of ion-exchanged metal cations. In addition, the effect of pore structure (pore size, channels and cavities, and dimensionality) on catalytic activity and selectivity was investigated.

Because bulky organic molecules or reaction intermediates are involved in the reaction between PhOH and TBA, dealuminated large-pore zeolites with FAU, BEA, and MOR topologies were chosen as catalysts in our investigation. It is known that, upon steaming under various conditions, the zeolites Y, Beta, and MOR yield a wide spectrum of acid site distribution. Moreover, extraction of framework aluminum results in the formation of mesopores in the zeolite crystals, which are thus made more accessible for reacting molecules.

2. Experimental

2.1. Preparation and characterization of catalysts

Zeolites Beta and USY, with various Si/Al ratios, were provided by the PQ Corporation. The parent mordenite MOR5.5 (Si/Al = 5.5) was purchased from Zeolyst International. Two dealuminated samples (Si/Al = 19 and 78), referred to in this study as MOR19 and MOR78, were obtained by steaming of the ammonium-exchanged mordenite in a flow reactor at 873 K and a partial pressure of water vapor equal to 3.2 kPa. A mild acid treatment of the dealuminated samples was applied in order to eliminate the soluble extraframework species, formed during the hydrothermal treatment (0.05 M HNO_3, 8 h, 333 K, 2 times).

The crystallinity of each sample was evaluated by XRD analysis on a CGR Theta 60 instrument using monochromatized Cu-K_α radiation. The sorptive characteristics of zeolites were determined by adsorption of nitrogen at 77 K, using a Micromeritics ASAP 2000 instrument. The acid properties were evaluated by the temperature-programmed desorption of ammonia (NH_3-TPD). Ammonia was first adsorbed at 373 K, and then the thermodesorption was carried out in a steam of He at a heating rate of 10 $\mathrm{K\,min^{-1}}$ up to 873 K. The amount of desorbed ammonia was monitored with a conductivity cell (TCD) and was measured by back titration (with HCl and NaOH).

2.2. Catalytic experiments

The catalytic experiments were carried out in a 50-ml glass batch reactor, equipped with a magnetic stirrer, a thermometer, and a condenser. The catalyst was activated by heating at 433 K and at a pressure below 1 Torr for 5 h just before the catalytic run. A typical batch consisted of 10 mmol of phenol (PhOH), 6 mmol of *tert*-butanol (TBA), 200 mg of catalyst, and 20 ml of CCl_4 (used as solvent). The temperature was maintained at 343 K and the speed of stirring was 800 rpm. Samples were withdrawn periodically and were analyzed by a GC-FID equipped with a capillary column (HP-5, poly(5% diphenyl–95% dimethyl)siloxane, 25 m × 0.2 mm, 0.33 µm film thickness). Products were identified by means of GC-MS and by comparing them with authentic compounds.

3. Results

3.1. Catalyst characterization

The samples of the USY, Beta, and MOR zeolites with different Si/Al ratios were characterized by various techniques. The main textural characteristics are summarized in Table 1, and the general features of the corresponding class of zeolites are given. X-ray diffraction showed that all the materials were highly crystalline.

The surface area (S_{BET}), the micropore volume (V_{micro}), and the mesopore volume (V_{meso}) were evaluated by means of the *t* plot, Dubinin–Raduskevich, and BJH methods, from nitrogen adsorption/desorption isotherms performed at 77 K. For each type of zeolite, the BET surface area and micropore volume agree well with reported data, and they decrease in the order USY > Beta > MOR [29–31]. The adsorption–desorption nitrogen isotherm shapes of dealuminated samples showed a hysteresis loop which has been attributed to the presence of mesopores [32]. A large portion of the mesopores was found in the Beta and USY zeolites. This portion

Table 1
Characteristics of zeolites used in phenol butylation

Catalyst	Si/Al	S_{BET} ($m^2\,g^{-1}$)	Pore volume ($cm^3\,g^{-1}$)		General features		
			V_{micro}	V_{meso}	Dimensionality	Pore size (nm)	SI
USY10	10	635	0.245	0.101	3D	Supercage: 1.18	21
USY21	21	750	0.257	0.165		Window: 0.74	
Beta15	15	616	0.199	0.140	3D	0.55 × 0.55	18
Beta25	25	611	0.195	0.162		0.76 × 0.64	
MOR5.5	5.5	432	0.195	0.022	2D	0.65 × 0.70	7.5
MOR19	19	454	0.193	0.041		0.26 × 0.57	
MOR78	78	482	0.184	0.083			

SI, spaciousness index [28].

Table 2
TPD of ammonia from USY, Beta, and MOR catalysts

Catalysts	T_{max} (K)	Amount of NH_3 ($mmol\,g^{-1}$) desorbed within certain temperature range (K)				$s/(w+m)$
		373–523 (w)	523–673 (m)	673–873 (s)	373–873 (total)	
USY10	423, 628	1.82	0.69	0.30	2.80	0.12
USY21	453, 623	1.32	0.56	0.22	2.10	0.12
Beta15	450, 678	0.63	0.85	0.42	1.90	0.28
Beta25	453, 673	0.53	0.80	0.37	1.70	0.28
MOR5.5	448, 743, 803	1.05	1.06	1.19	3.30	0.56
MOR19	436, 758, 803	0.58	0.55	0.67	1.80	0.59
MOR78	433, 755	0.26	0.35	0.39	1.00	0.64

is much smaller in the mordenites (Table 1). For each family of zeolites, the V_{meso} values increase as the Si/Al ratio increases, i.e., with the increasing degree of dealumination.

The acid properties of the samples were estimated by the thermodesorption of chemisorbed ammonia (NH_3-TPD). This technique provides general information about the number and distribution of the acid strength of the active sites. Two peaks, characterized by the maximal temperature T_{max} (Table 2), were observed in the NH_3-TPD spectra of the USY and Beta samples, whereas three peaks were detected for the MOR samples.

The amounts of desorbed ammonia were formally divided into three temperature regions to denote three types of acid site: (1) weak acid sites, ranging from 373 to 523 K, (2) moderate acid strength, ranging from 523 to 673 K, and (3) high acid strength, ranging from 673 to 873 K (Table 2). It was observed that ammonia desorption from the acid sites occurred mainly at the relatively low temperatures for the USY samples, at the intermediate temperatures for the Beta samples, and in the high temperature domain for the MOR samples.

These data and the maximal temperatures (T_{max}) show that the acid strength of the samples decreases in the order MOR > Beta > USY. These results agree with previously reported enthalpy measurements [33–35]. The overall amount of desorbed ammonia (Table 2) enables us to evaluate the concentration of the accessible acid sites. As expected, for each family of zeolite the concentration of the acid sites decreases as the Si/Al ratio increases. In the case of the samples with a relatively close Si/Al ratio, the total acidity decreases in the order USY21 > MOR19 > Beta25.

3.2. *Effect of zeolite type on catalytic activity*

In order to investigate the effect of the nature of the zeolite on the catalytic activity in the alkylation of phenol with t-butanol in the liquid phase, we tested the previously noted samples of USY, Beta, and MOR zeolites in this reaction, which was carried out at 343 K. As noted in the experimental part, the catalysts were activated at 433 K, under vacuum just before the catalytic run. Thus, no water was present on the fresh catalyst surface. We used the same solvent CCl_4 as in the alkylation of phenol over Y zeolite [18]. In addition, this aprotic nonpolar solvent was preferred since, as previously reported for the allylation of phenol over zeolite HBeta [36], aprotic polar solvents such as acetonitrile or THF influence both the catalytic activity (it decreases) and the catalytic selectivity (the phenyl allyl ether was formed as major product, $\sim$ 97 wt% yield). Furthermore, in the presence of the solvent the formation of polymerized product is less because of the effect of dilution. The experiments were carried out at a molar ratio of PhOH/TBA $= 1/0.6$ for two reasons: (i) to avoid the formation of large amounts of secondary products, such as the oligomers of isobutene, and (ii) to diminish the influence of the water formed by the dehydration of *tert*-butanol in situ. At the same time, the excess of phenol is small enough to have a crucial influence on the alkylation reaction.

The overall conversion of phenol versus the reaction time for all the tested catalysts is illustrated in Fig. 1.

As shown in Fig. 1, the phenol conversions in the presence of the USY and Beta zeolites are much higher than those obtained with the mordenites at the same reaction time. Differences in activity are also observed for the samples belonging to the same family. Thus, for each type of molecular

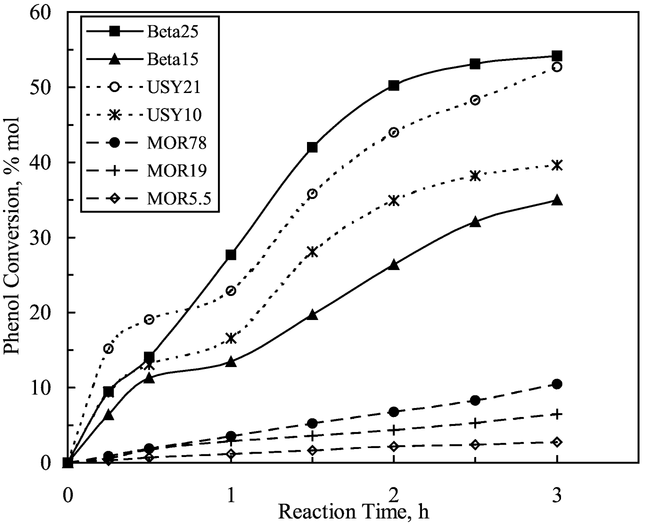
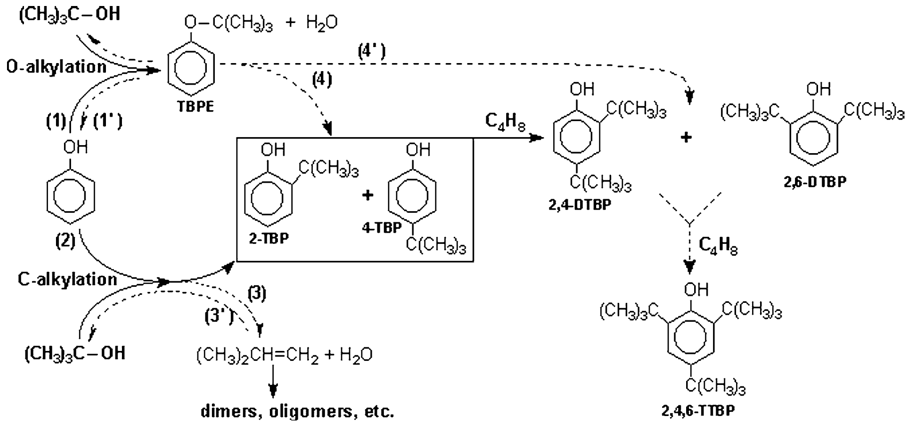


Fig. 1. Overall conversion of PhOH vs reaction time. $T = 343$ K, PhOH/TBA $= 1/0.6$ (mol/mol).



Scheme 1.

sieve, the phenol conversion is higher when the Si/Al ratio is higher.

These catalysts behaved similarly in the conversion of the alkylating agent. Furthermore, we observed that 3 to 6% of the initial TBA was involved in a series of secondary reactions such as the oligomerization of C_4 olefins (see Scheme 1, route **3**), as demonstrated by the presence of the isobutene dimers and trimers in the reaction mixture, determined by GC-MS analysis. i-Butene is the product of the acid-catalyzed dehydration of TBA.

3.3. Effect of zeolite type on catalytic selectivity

The main products of the catalytic butylation of phenol are *tert*-butyl phenyl ether (TBPE), *ortho*- and *para*-*tert*-butylphenol (2-, 4-TBP), and 2,4-di-*tert*-butylphenol (2,4-DTBP). Small amounts of 2,6-di-*tert*-butylphenol (2,6-DTBP), 2,4,6-tri-*tert*-butylphenol (2,4,6-TTBP) and 4-(2,2, 4-trimethylpenthyl)-phenol were also detected. C_8 and C_{12} olefins, the products of isobutene oligomerization, were also identified in the reaction mixture. No m-TBP formed on any of the tested catalysts. However, the distribution of reaction products was strongly affected by the type of zeolite, as will be shown later.

3.4. Phenol butylation over USY zeolites

Fig. 2 shows a typical evolution of product selectivity for the reaction between phenol and t-butanol carried out over USY catalysts.

In the early stages of the reaction (up to 1–1.5 h), on the fresh catalyst when the concentration of the alkylating agent is high, the main product is TBPE (only small amounts of C-alkylated products are formed), and its concentration reaches a maximum after approximately 1 h of reaction. As the conversion of phenol and t-butanol increases, a decrease in the yield of TBPE and an increase in the yield of TBP (*ortho* and *para* isomers) are observed. Moreover, *mono*- and *di*-C-alkylated phenols become the main products after 2 h of catalytic reaction. It is clear from this figure that TBPE is one of the primary products of the reaction, but it is subsequently converted by a rearrangement reaction or by hydrolysis. We will discuss this aspect in the next section, but it is important to state here that the direct alkylation on the C atom becomes the main reaction from this point on. Furthermore, as shown in Fig. 2, 2-TBP is the main C-monoalkylated product over the USY21 zeolite.

A similar behavior was observed when the reaction was carried out on the USY10 sample. Fig. 3 displays the product yields compared with the total conversion of phenol for this catalyst. As above, the formation of TBPE as the primary product is evident in the initial stage of reaction, and 2-TBP is the main C-alkylated product.

3.5. Phenol butylation over Beta zeolites

Fig. 4 shows the results of the reaction of phenol butylation, carried out in the presence of the most active catalyst of the Beta-type (Beta25).

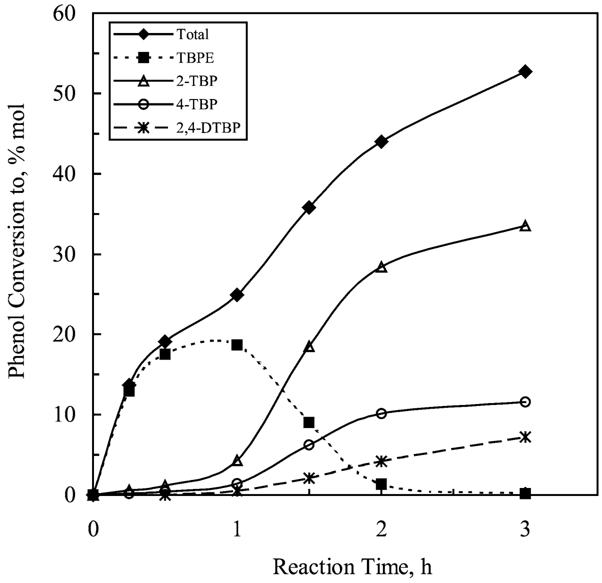


Fig. 2. Evolution of product selectivity over USY21 catalyst; $T = 343$ K, PhOH/TBA $= 1/0.6$ (mol/mol).

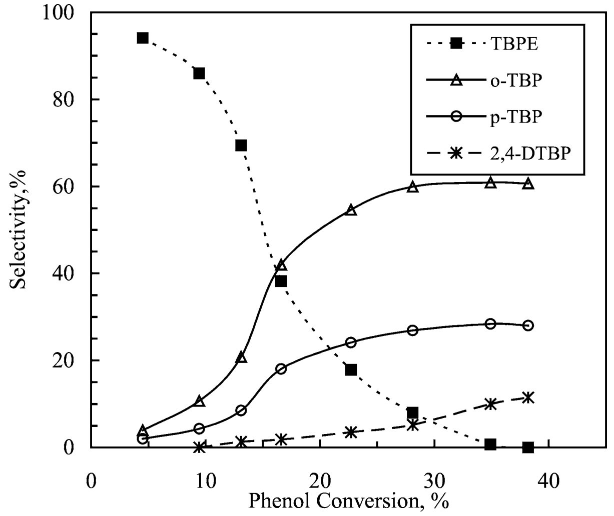


Fig. 3. Product selectivity vs overall phenol conversion on USY10; $T = 343$ K, PhOH/TBA = 1/0.6 (mol/mol).

The start of the reaction is similar to that in the presence of USY zeolites. Again the O-alkylated phenol (TBPE) is the main product in the early stages, but in this case the larger amounts of C-alkylated products form sooner than for the faujasites. As a consequence, the consumption of the ether is faster on the Beta catalysts, and the direct C-alkylation of phenol by TBA is more evident.

As regards the distribution of the reaction products, significant differences were observed between the two classes of zeolites, USY and Beta. Thus, the *para* isomer (4-TBP) is the main product in the presence of Beta25, and for the other samples of Beta, whereas the *ortho* isomer (2-TBP) is the main product when the butylation is carried out on USY catalysts.

The 4-/2-TBP ratio was constant for a long period of time for all the tested catalysts, which can be considered to be proof that no isomerization of the C-monoalkylated phenols takes place. This fact is clearly seen in Fig. 5, which illustrates the selectivity to 4-TBP vs the conversion of phenol for the Beta25 and USY21 samples.

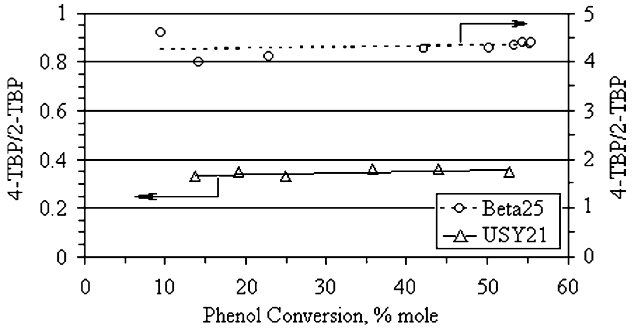


Fig. 5. Selectivity to 4-TBP vs the conversion of phenol; $T = 343$ K, Ph/TBA = 1/0.6 (mol/mol).

3.6. Phenol butylation over MOR zeolites

The mordenite-based catalysts behave differently compared to the zeolites BEA and USY (Fig. 1). First, the conversions obtained on mordenites are smaller than on the other zeolites. Fig. 6 shows the evolution of product selectivity for a longer reaction time (8 h) for MOR78 zeolite, the most active catalyst in the series.

The evolution of reactions in the presence of this catalyst is close to that observed for the Beta and USY zeolites, but the reaction rates for the chemical transformations are lower, especially in the presence of samples MOR5.5 and MOR19. Thus, after 18 h of reaction in the presence of MOR5.5, the phenol conversion was 10.4%, and the molar ratios between TBPE, 2-TBP, and 4-TBP were 20:1:2.5. Only traces of dialkylated products were formed in this case.

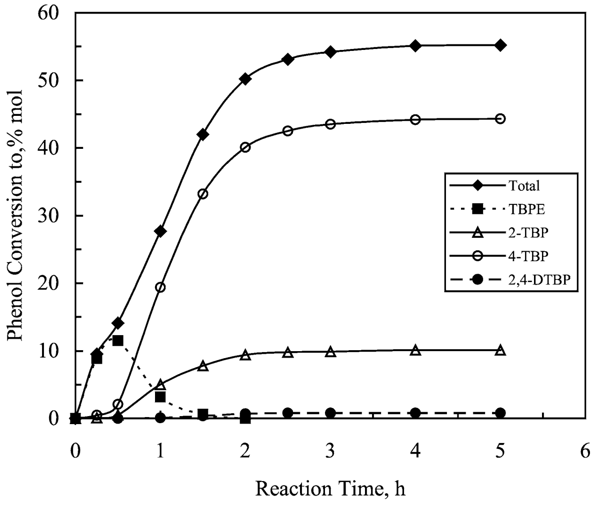


Fig. 4. Evolution of product selectivity over Beta25 catalyst; $T = 343$ K, PhOH/TBA = 1/0.6 (mol/mol).

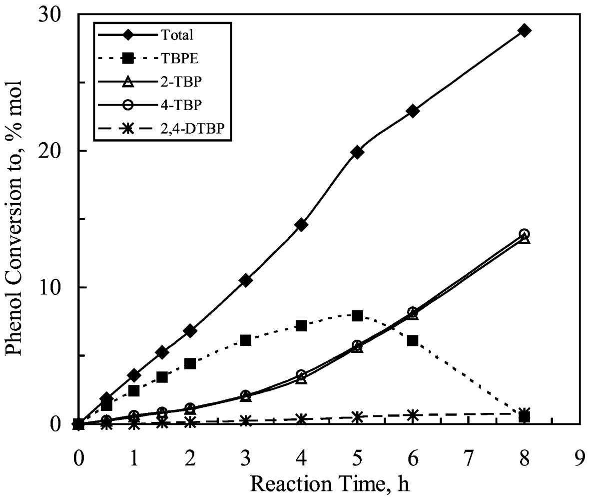


Fig. 6. Evolution of product selectivity over MOR78 catalyst; $T = 343$ K, PhOH/TBA = 1/0.6 (mol/mol).

4. Discussion

The most important problem areas with respect to catalytic alkylation of phenols are: (i) catalytic activity, (ii) the ratio between O- and C-alkylation, and (iii) catalytic selectivity towards the desired C-alkylated phenol, with regard to the structural and acid properties of the catalysts.

4.1. Catalytic activity

As noted in the Introduction, various catalytic systems have been used for the alkylation of phenol by *tert*-butanol, and the molecular sieves represent an important group of catalysts that activate this reaction [18–26].

Our results, of the liquid-phase alkylation of phenol with TBA on three different types of zeolites, showed very good catalytic activity for the Beta and USY zeolites but low catalytic performance for the mordenite samples (Fig. 1), although they have the same large 12-membered ring pores. The experimental results indicate the following order of total catalytic activity: Beta 25 > USY21 > USY10 > Beta15 >> MOR78 > MOR19 > MOR5.5. To explain these differences, two main categories of properties are taken into account:

- acid properties (the concentration of acid sites and the acid strength of the sites),
- diffusional properties, which are determined by the pore architecture.

These properties also determine the catalytic selectivity.

The reactions involved in this process of alkylation are the acid-catalyzed reactions. As indicated above (Table 2), the mordenite-based catalysts are characterized by an important total acidity and their active sites have an acid strength higher than the USY or Beta zeolites. So, it could be expected that MOR-based catalysts will show a catalytic activity in the initial stage of the reaction comparable with those of the other catalysts (e.g., Bea or USY), at least with fresh activated catalyst surfaces. Therefore, the differences between the mordenite samples and other catalysts could be attributed especially to their different structure of pores, which result in the different diffusion rates for the reactants, the intermediates, and the products. It is known that the problems of mass transfer generated by the diffusional limitations are more important for the liquid-phase reactions than those of the gas-phase reactions.

Zeolites Beta, USY, and MOR are defined as having a 12-membered ring pore system, but they differ as dimensionality. Zeolite Beta has a three-dimensional interconnecting pore system with pores of 0.55×0.55 and 0.76×0.64 nm, whereas USY has a three-dimensional interconnecting pore system with supercages of 1.18 nm connected by circular 12-ring 0.74-nm windows. Mordenite has a bidimensional pore system, with parallel circular 12-ring channels (0.65×0.70 nm) and elliptical 8-ring channels (0.26×0.57 nm), but practically it functions as a monodimensional pore system since the 8-ring channels do not allow access of the usual molecules.

As known, the spaciousness index (SI) is an important criterion for the characterization of 12 MR pore systems [37]. SI is defined as the ratio of the yields of isobutane and n-butane in the cracking reaction of C_{10} naphtene [38] and it is based particularly on restricted transition state shape selectivity. SI values estimated for Y, Beta, and MOR are 21, 18, and 7.5, respectively [28]. Thus, it could be that the mass transfer by the pore system of mordenites is more limited than in the case of USY and Beta samples and this supposition can explain the differences of reaction rates noted above (Fig. 2).

Moreover, for each type of zeolite, the catalytic performances increase with the increase of the fraction of mesopores (Table 1). Consequently, it could be considered that some limitations are also present in the case of USY and Beta samples having a more reduced mesoporosity, but these limitations are less important with regard to those observed for MOR zeolites.

It is known that increasing the framework Si/Al ratio has an effect not only on the acidity and mesoporosity but also on the adsorption properties of the zeolite. In a reaction system that involves reactant with different polarities, as in our case, the hydrophobicity/hydrophilicity of the zeolite were important factors, which might influence the catalytic performances. As indicated in Fig. 1, the samples with high hydrophobic character (high Si/Al framework ratio) are the most active catalysts due to their improved adsorption properties for nonpolar molecules.

4.2. O- vs C-butylation

The catalytic alkylation of phenol with alcohols gives rise to two distinct classes of products depending on where the alkyl group alkylates, as illustrated for the alkylation of phenol with *tert*-butanol by Scheme 1 (routes **1** and **2**).

The formation of O-alkylated products depends both on the intrinsic properties of the alcohol (e.g., its reactivity) and on the structural and acid–base properties of the catalysts. Methanol is the most reactive alcohol and anisole is easily obtained and is more stable than other O-alkylated products of higher alcohols. The O-alkylated product is more difficult to obtain as the hydrocarbon chain of the alcohols increases, mainly due to the high reactivity or instability of the resulting ether. For instance, few studies reported the synthesis of TBPE by the alkylation of phenol with t-butanol because this reaction leads to high yields only at low temperatures. Gurvici et al. [3] obtained a 60% yield of TBPE in the alkylation of phenol with i-butene in the presence of H_2SO_4 at 288 K, but only 20% at 323 K. Similarly, Corma et al. [18] found that the alkylation of phenol by TBA over the solid acid HNa-Y zeolites at 303 K occurs both at the O-atom and at C-atoms, but that the O-alkylation had a relatively high selectivity (55–76%), whereas ring alkylation only oc-

Table 3
Product selectivity in phenol alkylation with TBA (reaction time = 3 h)

Catalyst	V_0	PhOH conversion	Selectivity (%mol)					4-/(2 + 4)-TBP
	(mmol TBPE/(h g_{catal}))	(%)	2-TBP	4-TBP	2,6-DTBP	2,4-DTBP	2,4,6-TTBP	(×100)
USY10	27.5	37.7	60.7	27.3	0.5	11.2	0.3	31.0
USY21	33.5	52.7	63.0	23.0	0.6	13.1	0.3	26.7
Beta15	19.4	35.0	16.9	82.5	0	0.6	0	83.0
Beta25	26.2	54.2	18.3	80.3	0	1.4	0	81.4
MOR78[a]	2.0	28.8	48.1	49.1	0	2.8	0	50.5

[a] Reaction time = 8 h.

curred at higher temperatures (318–353 K). However, Anand et al. claim the formation of *tert*-butyl phenyl ether in the gas phase, even at 373 to 473 K [27].

The results obtained under our conditions indicate that, on all types of catalysts, TBPE is the main product of the reaction between PhOH and TBA in the initial stage of the reaction. Moreover, according to the Figs. 2 and 4, it may consider that TBPE is the main product (if not the only product) for this stage of reaction. From the experimental data the initial rates of TBPE forming were determined and their values (V_0) are included in Table 3. Also, Table 3 collects the product distributions obtained for various catalysts, these will be latter discussed.

In the case of the zeolites exhibiting high activity (i.e., Beta, USY) the highest V_0 values were obtained over the most acidic USY samples (Table 2). Based on these results, we can state that in the early stages of the reaction the reversible O-alkylation occurs at a high rate due to its low activation energy on almost the all acid sites (independent of its acid strength). We consider that this analysis of the acidity–activity relationship is valid for the early stages of the alkylation reaction when the acid properties of the fresh activated surfaces are not yet altered by other molecular species formed during the reaction like the water molecules. In the case of MOR samples, when the reaction rate is controlled by diffusion, the initial rate is smaller, even for the samples with acidity higher than those of the USY and Bea zeolites.

However, as the alkylation reaction proceeds the water molecules are formed and accumulated on the surface influencing the nature and the strength of the catalytic sites. These changes are difficult to measured but, indubitably, they will influence the reaction rate, the reaction pathways, and the catalytic selectivity.

Water plays multiple roles for this system of reaction:

- it changes the nature of active sites and their environments,
- it shifts the reaction equilibrium (especially in the case of the eterification reaction),
- it competes for the active sites with other species existing in the reaction medium.

In order to understand the role played by the water, an additional alkylation experiment was carried out on a hydrated USY21 sample (referred as USY21-H). A water-saturated air stream was passed over 200 mg catalyst placed in a tubular reactor, for 2 h at room temperature. Then, the butylation reaction was carried out in a batch reactor, using USY21-H as catalyst, and under the experimental conditions described in the experimental part. The results of these experiments are given in Fig. 7.

For comparison, the total conversion of PhOH, obtained over dried USY21, is included in this figure. It is clear from this figure that the TBPE formation is suppressed to a considerable extent over the hydrated sample. This explains why on the dried catalysts as the alkylation reaction proceeds and the water molecules accumulate on the surface the formation of TBPE is progressively diminished until it is suppressed (Figs. 2–4). From Fig. 7 two other aspects could be evidenced:

- the induction period that precedes the direct C-alkylation of phenol is also present in the case of the USY21-H sample. Moreover, this period is longer for the hydrated sample than for USY21. Also, the phenol conversion reaches approximately the same value, but after a longer period of reaction (5 h against 3 h).
- After the C-alkylation starts, the overall rate of reaction strongly increases and the shape of the reaction curves

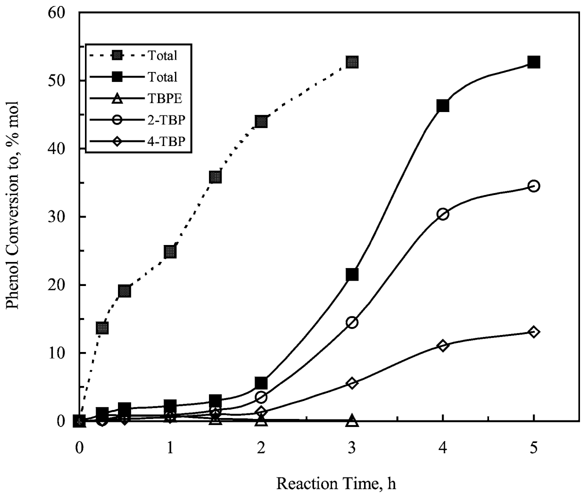


Fig. 7. Evolution of product selectivity over hydrated USY21 catalyst; $T = 343$ K, PhOH/TBA = 1/0.6 (mol/mol); (– – –) overall conversion of PhOH on dried USY21 sample.

becomes similar to those obtained for the dried catalysts (Fig. 2). Also, we could note that the ratio between the two TBP isomers is the same for both samples.

According to Scheme 1 and Figs. 2 to 4, for the formation of mono C-alkylated phenols two routes of reaction are possible: (i) the TBPE rearrangement and (ii) the direct alkylation of the aromatic ring. It is known that TBPE easily rearranges to C-alkylated phenol derivates [39] only by simple heating at 473 to 543 K or by contact with an acid catalyst (Brönsted or Lewis acids). The intramolecular rearrangement of alkoxybenzene leads preferentially to the *ortho*-alkylated product [40]. Consequently, the rearrangement reaction during the alkylation process will change the distribution of the alkyl phenols. However, as Figs. 2 and 7 show, the ratio between *ortho*- and *para*-TBP is the same both in the presence and in the absence of ether (i.e., in the presence of the hydrated or dried samples). Therefore, it may be that TBPs are obtained by the rearrangement of TBE only in a small amount, and the most part of TBE is hydrolyzed to phenol (Scheme 1, route **1**′).

Under these circumstances, we could affirm that the direct C-alkylation is the main route to TBPs formation. At the same time, it difficult to explain why the irreversible C-alkylation takes place after a long period of induction.

4.3. Selectivity to C-alkylated products

In previous studies of the butylation of phenol the selectivity to C-alkylated products was analyzed in relation to the porosity and acid properties of the catalyst. The alkylation reactions carried out in the gas-phase system (at high reaction temperature) in the presence of catalysts with weak [24], moderate [19,22,23] or strong acid sites [20] are suitable for the formation of *para*-C-alkylated isomer. The increased selectivity to the *para* isomer of *tert*-butyl phenol (thermodynamically more stable that *ortho* isomer) was explained as being the result of several consecutive reactions such as the isomerization and disproportionation, the dealkylation or the transalkylation involving mono- and poly-alkylphenols [20,23]. In the liquid phase, under gentle conditions of reaction, the process is less affected by its thermodynamics; thus, the distribution of reaction products is mainly controlled by the kinetics or by the diffusion processes. The secondary reactions above noted do not proceed under such conditions. Some earlier reports support this assertion. Thus, Yoo et al. [41] examined the product distribution in relation to the pore size and acid properties of the zeolites. They found that in the liquid-phase butylation of catechol, the selectivity to 4-t-butyl catechol did not depend on the acidity of the ZSM-5, USY, and BEA zeolites, but that it was controlled by the size of the zeolite pores and its structure. Liu et al. [42] found a *para*-selective effect for Beta zeolites in liquid-phase alkylation of naphthalene with *tert*-butanol.

For a better understanding of the way in which the nature of the catalyst can influence the product distribution in our reaction system, the experimental data obtained after 3 h of reaction in the presence of the USY and Beta catalysts are listed in Table 3.

After this period, TBPE is almost completely converted and the ratio between the C-alkylated products remains more or less constant. In comparison, the data obtained for MOR78 (but after 8 h of reaction, when no significant amounts of ether are evident) are included in this table.

From these data, the following remarks can be made:

- For monoalkylated products the ratio between *ortho* and *para* isomers strongly depends on the type of catalyst. Thus, high *para* selectivity (4-TBP/(2-TBP+4-TBP)) was observed for all the Beta samples, whereas USY zeolites are not *para* selective. In the case of the MOR78 zeolite, the 4-TBP/2-TBP ratio is close to unity. The *para* selectivity was 68% for MOR19 and 73% for MOR5.5. These data are not reported in Table 3.
- The *para* selectivity of each type of zeolite also depends on the Si/Al ratio. The *para* selectivity is higher when the Si/Al ratio is lower.
- Contrary to Beta and MOR, the USY zeolites favor the formation of large amounts of dialkylated products. Bulky compounds such as 2,6-DTBP and 2,4,6-TTBP are obtained only on USY catalysts.

It is accepted that when the product is not thermodynamically controlled, both the electronic and the steric factors are very important for the alkylation reactions in heterogeneous catalysis. Generally, the electrophilic substitution may take place in the *ortho* and *para* positions of the phenyl ring. It is difficult to predict how much of the product will be the *ortho* isomer and how much the *para* isomer. On a purely statistical basis, there would be 67% *ortho* and 33% *para*, since there are two *ortho* position and only one *para*. Moreover, the presence of phenolic group kinetically favors *ortho*-alkylation [43].

The electrophilic attack of the *tert*-butyl ion at the *ortho* position of the aromatic ring leads to formation of bulky σ-intermediates, which can be accommodated in the large cages of the ultrastable zeolite Y, one of the most open microporous zeolitic structure. Thus, high amount of 2-TBP is formed in presence of USY samples. The fact that bulky compounds as di-*tert*-butyl phenols are formed particularly on USY is also due to their lower geometrical restrictions.

The selective formation of 4-TBP over Beta (0.76 × 0.64 and 0.55 × 0.55-nm interconnected channels, absence of supercages) and MOR (0.65 × 0.70-nm monodimensional channels) could be attributed to the pore-size effect of these zeolites which are capable of limiting the formation of isomers with relatively large dimensions.

Furthermore, if the *para* selectivity is analyzed taking into account each class of zeolites, and particularly for MORs, it could be observed that this selectivity increases with the decrease of the fraction of mesopores.

5. Conclusions

Alkylation of phenol with *tert*-butanol over a series of USY, Beta, and MOR zeolites, in the H^+ form, was studied in a batch reactor. Due to their improved diffusion properties, USY and Beta samples catalyze more efficiently than MOR zeolite in this reaction which involves bulky organic molecules.

The role played by water is very important. Over a dried catalyst surface, *tert*-butyl phenyl ether is the main product of alkylation, but it is unstable under catalytic conditions and easily converted. Direct C-alkylation of phenol becomes the main alkylation reaction after the accumulation of water molecules on the catalyst surface.

The geometric constrictions of the catalysts significantly influence the C-alkylated phenol distribution. Thus, the formation of bulky di-*tert*-butyl phenols occurs especially in the large cavities of USY zeolite. High selectivity to 4-TBP is achieved in the presence of Beta samples ($\sim 75\%$), while high selectivity to 2-TMB is obtained when USY samples activate the alkylation process.

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