

Alkylation of benzene by propene on a series of Beta zeolites: toward a better understanding of the mechanisms

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Abstract

Alkylation of benzene with propene has been investigated on a series of H-Beta zeolites with different Si/Al ratio: 10, 35 and 66, using different techniques such as FTIR, ¹³C NMR and catalytic testing. It has been shown that H-Beta zeolite (Si/Al ratio = 10) is a very active catalyst for this reaction with propene, but it leads also to fast oligomerization even at lower reaction temperatures. ¹³C NMR experiments have demonstrated for the first time that the reaction of alkylation is already complete at -80°C on these catalysts. Dealuminated H-Beta zeolites are less active but lead to less aromatic by-products (especially *n*-propylbenzene) and the deactivation due to the coke formation is reduced. The high ratio of benzene/propene favors the formation of cumene and suppresses the oligomerization of propene. Triisopropylbenzene (TIPB) can also be formed at low temperatures ($< 100^{\circ}\text{C}$) and then is transformed by transalkylation into diisopropylbenzene (DIPB) at higher temperatures ($> 130^{\circ}\text{C}$). The present work reveals that the alkylation of benzene by propene occurs via an Eley–Rideal type mechanism. The apparent activation energy for this reaction has been determined and shows to decrease as the Si/Al ratio of H-Beta zeolites increases. The relatively low apparent activation energies obtained for this reaction on a series of H-Beta zeolites studied suggests that it exists a diffusion step of reactants and products between the silanols of the Beta zeolite. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Alkylation of benzene with propene is an interesting industrial reaction because it leads to cumene, which is an important current interme-

diated in the production of phenol and acetone. Moreover, in the coming years, the price of benzene is expected to decrease since environmental regulations demand lower proportions of this aromatic in the gasoline pool and the need for phenol is increasing from year to year [1]. The industrial production of cumene is based on the use of Friedel-Crafts [2] or solid phosphoric acid (SPA) [3] catalysts. However, the alkylation over zeolites gained increasing interest compared to the highly contaminating and cor-

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rosive catalysts usually employed. Several zeolites are reported to be able to catalyze this reaction [4–7]. Two commercial cumene processes have been developed by Mobile and CDTECH, respectively. The first one operates in a fixed bed reactor system using ZSM-5 zeolite as catalyst [8,9] and the second in a catalytic distillation column reactor using Y-type zeolite [10]. However, the rapid ageing of zeolite catalysts is still an essential problem to resolve. For instance, faujasite catalysts have been employed in alkylation reactions but their low resistance to coking is due to their supercages (12 Å), which favor the accumulation and enlargement of coke precursors. Lately, DOW has reported the development of a new cumene process based on a highly dealuminated Mordenite [11]. Recently, Beta zeolite has been shown to be a potential catalyst for the alkylation of benzene [12–16] and would be used in the new industrial process [14]. In contrary to faujasite zeolite catalysts, Beta zeolite possesses smaller channels intersections (about 9 Å) and comparable channel diameters. Bellussi et al. [14–16] have reported that zeolite Beta is more active and more selective than Y zeolite in the liquid phase alkylation of benzene with propene. An industrial process using Beta zeolite is indeed in operation in Sardegna. However, although the separation of products is often difficult, most of studies on this reaction were carried out in liquid phase conditions since this reaction can be operated at moderate temperatures. This reaction performed in gas phase conditions is rarely reported. Furthermore, the real mechanism of cumene formation into the zeolite is still unclear in spite of some molecular mechanics calculations and it is of importance to achieve the best preparation of the catalyst and the reaction conditions. In this work, the alkylation of benzene with propene has been investigated on a series of H-Beta zeolites using in-situ techniques (FTIR and NMR) and a catalytic test. The understanding mechanism of this reaction into the zeolite is the main aim of the work.

2. Experimental

2.1. Preparation of the catalysts

The starting Beta zeolite (Si/Al ratio = 10) was synthesized in our laboratory in alkaline medium in the presence of TEOAH according to the procedure of Cambior et al. [17,18]. The chemical formula of this zeolite, obtained from elementary analysis, is given for a unit cell of 64 T atoms as: $\text{TEA}_{6.4}\text{Na}_{0.6}\text{Al}_{5.4}\text{Si}_{58.6}\text{O}_{128} \sim 10\text{H}_2\text{O}$. The zeolite precursor was calcined at 550°C in air for 10 h to remove TEA, followed by an ion exchange with a solution of NH_4NO_3 (2 M, 70°C, 5.5 h) to give NH_4 -Beta. The exchanged sample was further calcined (550°C, 4 h in air) to give the protonated Beta zeolite [19]. Two other catalysts were prepared by dealumination of the NH_4 -Beta sample in the $(\text{NH}_4)_2\text{SiF}_6$ (0.5 M, 80°C, 3 h) and the HCl solution (0.2 M, 80°C, 3 h), respectively. These three H-Beta catalysts have Si/Al ratios of 10, 25 and 66, and labeled as H-Beta 1, 2 and 3, respectively.

2.2. Characterization of the catalysts

The crystallinity and phase purity of the zeolites were determined by X-ray diffraction (XRD, Philips PW 1710) with Cu K α radiation and scanning electron microscopy (SEM, Philips XL 20). The XRD powder patterns of as-synthesized sample and two dealuminated samples are same as those published previously [20,21] and show very good crystallinity (Fig. 1). This suggests that the dealumination treatments do not provoke a destruction of zeolite framework. The crystals are well defined and spherical shaped with crystal size of around 300 nm (Fig. 2). The amount of TEA occluded in as-synthesized sample was measured using differential thermal analysis (DTA) and differential scanning calorimetry (DSC) (Setaram thermogravimetric analysis TG–DTG–DSC 111 coupled with an ammonia Metrohn titrator). The

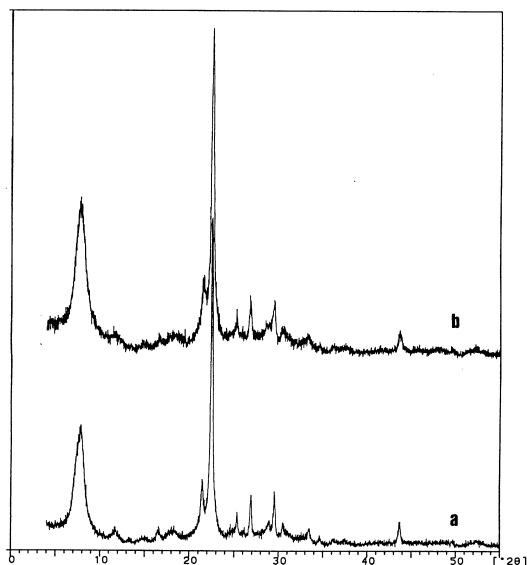


Fig. 1. XRD powder patterns of H-Beta 1 (a) and H-Beta 3 (b).

details of the procedure adopted for this apparatus used have been described elsewhere [19].

2.3. Alkylation of benzene with propene

2.3.1. FTIR studies

Self-supported wafers were pressed from 20 mg of zeolite powder under a pressure of 6 tonnes/cm² and then placed with a sample holder inside a Pyrex cell with two NaCl windows, which allowed pretreatment (1: 450°C in air for 6 h; 2: 450°C in vacuum < 10⁻⁶ Torr for 4 h), introduction of reactants and recording of the spectra. The different acid sites present in our zeolite catalysts were also analyzed by FTIR using Perkin-Elmer FTIR Spectrum 2000 Spectrometer.

2.3.2. ¹³C NMR study

Propene labeled in 2 was used in the present work. The zeolite samples (50 mg) were packed into NMR cells. After 6 h heating in air at 400°C, the catalysts were evacuated for 4 h (vacuum < 10⁻⁶ Torr) and cooled down to room temperature before introduction of reactants. An amount of benzene of 8 molecules/unit cell of zeolite and 1 molecule/unit cell of

propene were introduced into the cell in the way described as follows. A known amount of benzene (8 molecules/unit cell) was first introduced onto the zeolite wafer followed by the addition of a desired amount of propene (1 molecule/unit cell). To avoid any reaction at room temperature before recording the NMR spectra, propene was introduced into the cell at liquid nitrogen temperature. The samples were kept in liquid nitrogen during sealing the capsules and till they were introduced into the NMR apparatus (Bruker MSL-400) operating at 100.6 MHz. The MAS NMR study was achieved using high-power gated proton decoupling with suppressed NOE effect (90° pulse, recycling delay 4 s).

2.3.3. Catalytic tests

These were performed in a plug flow microreactor operating at atmospheric pressure. The quantities of benzene introduced were controlled by a cryostat with fixed N₂ flow and propene were controlled by mass flow meters. 50 to 100 mg of catalyst were first calcined in situ in microreactor in a flow of dry O₂ for 6 h at 450°C (heating rate: 3°C/min) and purging with N₂ for 5 h at 450°C. The products were analyzed quantitatively by gas chromatography (Perkin-Elmer Autosystem XL equipped with a FID detector and a semicapillary column Heliflex-Alltech AT-WAX) and qualified by GC-MS.

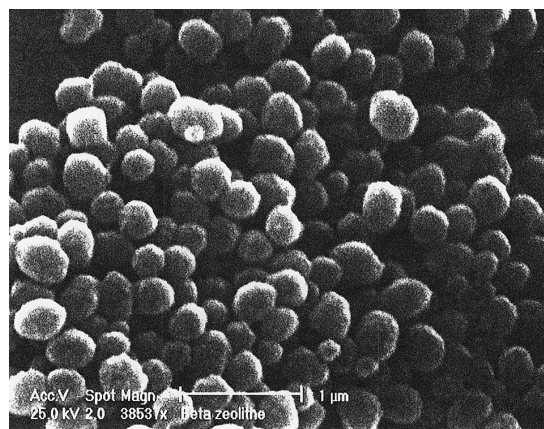


Fig. 2. Micrograph of as synthesised Beta zeolite by SEM.

The conversion is the percentage of propene transformed and the selectivity for a product corresponds to the percentage of this product on the total amount of reaction products. The apparent activation energy is obtained by means of Arrhenius equation.

3. Results and discussion

3.1. Characterization of the catalysts

3.1.1. Amount of TEA occluded in as-synthesized sample

The TG–DTG–DSC curves of the as-synthesized Beta zeolite under dry helium flow are reported in Fig. 3. It should be noted from the elementary analysis that there is an excess of compensating cations ($\text{TEA}^+ + \text{Na}^+$) relative to the amount of AlO_4 . This is due to the presence of a large number of SiO^- defect groups of the Beta zeolites [19,22] or because of the presence of TEAOH molecules in Beta zeolite [17,18,23]. The knowledge of the amount of each species gives access to the number of Brønsted acid sites. Three distinct weight endothermic loss ranges (Fig. 3) at 25–190°C (I), 190–400°C (II) and 400–540°C (III) are observed and correspond to the desorption of water (I), the degradation of TEA^+ species associated with SiO^- and with OH^- (II) and the degradation of TEA^+ associated with the framework (Si-O-Al^-

group of Beta zeolite (III) [19]. The number of TEA^+ associated with SiO^- or OH^- and that associated with the framework (Si-O-Al^-), are obtained to be 2.0 and 4.4 per unit cell, respectively. The total number of TEA cations per unit cell present in as-synthesized zeolite obtained from thermal analysis is therefore equal to 6.4, which is very close to the number obtained from elementary analysis.

3.1.2. Hydroxyls in the three H-beta zeolites

FTIR analysis of the different acid sites of the zeolites used was made. Fig. 4 depicts the hydroxyl stretching vibration range of 4000–3000 cm^{-1} of three H-Beta zeolites. The spectrum of the starting zeolite (Fig. 4a) shows four different OH groups at 3612, 3663, 3745 and 3784 cm^{-1} . The hydroxyls that give rise to the 3745 cm^{-1} band have been previously assigned to the terminal weakly acidic Si–OH groups [19,24]. The peak at 3612 cm^{-1} corresponds to the bridging framework Si–OH–Al groups. The very small bands at 3784 and 3663 cm^{-1} have been attributed, respectively, to the Al–OH species (slightly acidic) being near to SiOH groups generated when Al leave the framework, and the hydroxyls associated with extraframework aluminium [19,25].

The acidic Si–OH–Al groups at 3612 cm^{-1} are more important in intensity for the sample H-Beta (Si/Al = 10). The Si–OH–Al peak decreases in intensity with increasing Si/Al ratio (Fig. 4b and c). The peaks at 3782 and 3663 cm^{-1} disappear in two dealuminated samples (Fig. 4b and c). However, the band at around 3745 cm^{-1} corresponding to silanols is broadened and shifted to lower wavenumbers, 3742 cm^{-1} for the sample having a Si/Al ratio of 35 and to 3735 cm^{-1} for the sample with a Si/Al ratio of 66. The broadness of this peak stems from the creation of more silanols in the framework after dealumination and the interaction between these silanols. The slight shift toward lower wavenumber suggests a slight increase in acidity of these sites. The disappearance of the

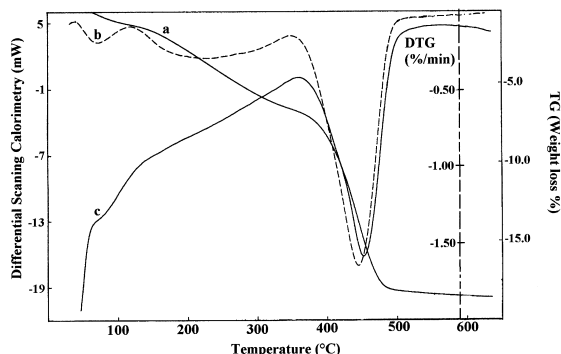


Fig. 3. (a) TG, (b) DTG (dashed line), (c) DSC curves of the as-synthesised Beta zeolite (He, 10°C/min).

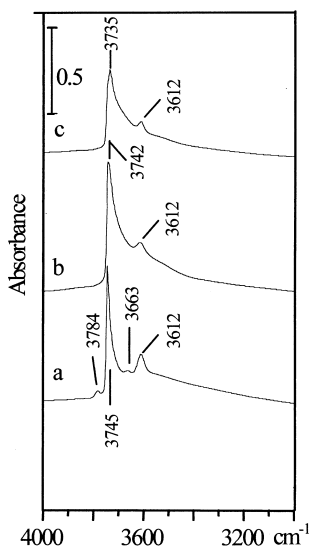


Fig. 4. IR absorbance spectra of the series of H-Beta 1(a), H-Beta 2 (b) H-Beta 3 (c) after pretreatment at 450°C in oxygen and then in vacuum.

peaks at 3748 and 3633 cm^{-1} after dealumination confirms their origin related to the Al and that an acid leaching can remove these species [19,25].

3.2. Study of the alkylation of benzene by propene

A detailed study of the alkylation of benzene by propene with FTIR has been described elsewhere [26]. In-situ FTIR studies have shown that H-Beta zeolites, especially the sample with a ratio Si/Al of 10, are very active for the alkylation of benzene with propene but these catalysts lead also to fast oligomerization at low temperature and to the formation of other aromatics for the more active system. The adsorption of propene alone demonstrates the oligomerization that occurs already at very low temperatures ($\sim -50^\circ\text{C}$). This is consistent with the previous reports by Haw et al., showing that propene is very mobile and reactive on zeolite catalysts even at temperatures below 0°C [27]. For a longer time and higher temperature ($> 50^\circ\text{C}$) some coke is also formed. However, the adsorption of benzene and propene in different

ratios shows the quick alkylation of benzene to cumene at very low temperatures ($\sim -50^\circ\text{C}$) and less oligomerization is observed for the higher benzene/propene ratio. Moreover, whatever the ratio of benzene/propene used, the lower quantity of propene should be used to have a higher selectivity of cumene and to reduce the oligomerization. These IR results will guide us to choose better the reaction conditions for ^{13}C NMR study and catalytic testing.

3.2.1. ^{13}C NMR study

This was used to obtain the temperature at which the alkylation takes place on the more dealuminated and less active zeolites. The temperature of the zeolite sample during and after preparation was maintained at liquid nitrogen temperature till the sample was introduced into the NMR apparatus at -80°C . The spectrum (Fig. 5), which was taken immediately at static condition after introduction of the sample adsorbed benzene and propene, shows that the reaction of alkylation was already complete and all the propene molecules introduced are consumed because no labeled propene remains observable, only a peak at 128.5 ppm, which can be attributed to benzene molecules and a broad and intense band centered at 34.4 ppm, which

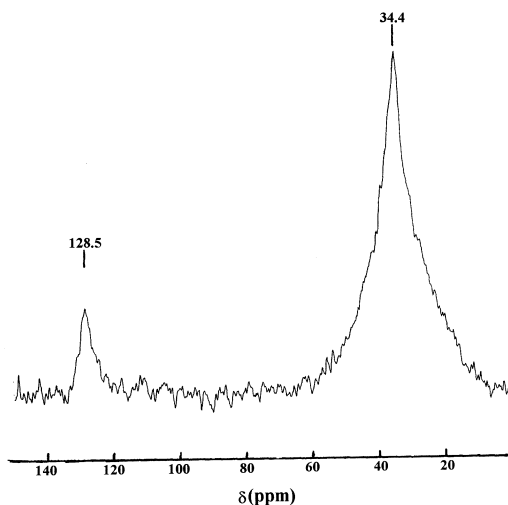


Fig. 5. ^{13}C MAS NMR spectrum of species present in H-Beta 3 sample (Si/Al = 66) after reaction at -80°C with Bz/Prop ratio = 8:1 (in molecules per unit cell).

corresponds to cumene C- α are present. The rapid and complete conversion of propene into cumene at 25°C upon contacting with benzene was previously observed by Ivanova and Derouane on HZSM-11 zeolite catalyst with a benzene/propene ratio of 9.0 in molecule using ^{13}C MAS NMR technique [28]. However, the present work indicates very clearly for the first time that the alkylation of benzene by propene occurs already at -80°C .

The reaction temperature of the sample was increased to 200°C ex-situ in a furnace and this temperature was maintained for 1.5 h to observe the formation of possible secondary aromatic products over H-Beta 1 (Fig. 6a) and H-Beta 3 (Fig. 6b). At this time, the ^{13}C MAS NMR technique was applied, and the NMR rotor was run at 3.8 kHz and all the spectra were recorded at room temperature. The formation of cumene on zeolites is actually often accompanied by its isomerization to *n*-propylbenzene [4,5,12,28–31] at higher temperatures. This latter product is considered as an undesired by-product with respect to further processing of cumene to phenol and acetone. Therefore, it is interesting to study the effect of the Si/Al ratio on the isomerization of cumene. The relative quantities calcu-

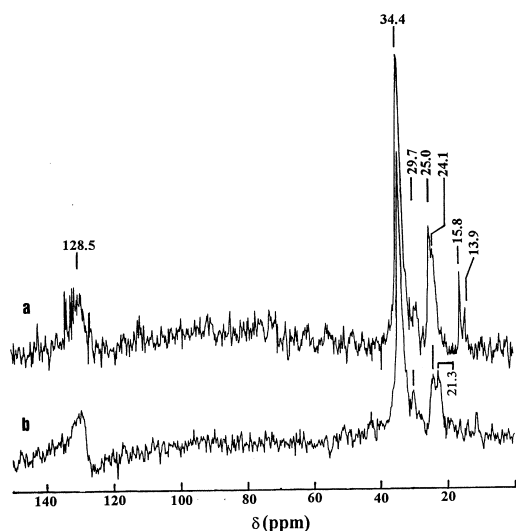


Fig. 6. ^{13}C MAS NMR spectra of species present in (a) H-Beta 1 and (b) H-Beta 3 after reaction at 200°C for 90 min and Bz/Prop ratio = 8:1 (in molecules per unit cell).

Table 1

Relative quantities of ^{13}C -labeled products resulting from cumene reaction at 200°C for 1.5 h on H-Beta 1 (a) and H-Beta 3 (b) (Bz/prop ratio = 8.0)

Products of reaction at 200°C	δ_c in ppm [33]	Intensity of ^{13}C MAS NMR signals	
		H-Beta 1 (Si/Al = 10)	H-Beta 3 (Si/Al = 66)
Benzene	128.5	medium	medium
Cumene C- α	34.4	very high	very high
Ethylbenzene C- α	29.7	low	low
<i>n</i> -Propylbenzene C- β	25.0	medium	^a
Cumene C- β	24.1	medium	medium
Toluene C- α	21.3	^a	medium
Ethylbenzene C- β	15.8	medium	^a
<i>n</i> -Propylbenzene C- γ	13.9	low	^a

^aNot detectable.

lated from the spectra of Fig. 6 of labeled products are reported in Table 1. Previous works [29] over HZSM-11 indicated the formation of the products by different mechanisms. The primary product from cumene was *n*-propylbenzene, which was then transformed via scrambling and fragmentation to toluene, ethylbenzene. Beyer and Borbely [32] have suggested that cumene isomerization proceeds more likely via two kinds of intermolecular transfer route. The intermolecular isomerization may occur: (1) through a bimolecular transition state in which the aromatic rings are bridged by an isopropyl group (route 1); or (2) by isopropyl group cleavage, followed by the formation of a cyclopropenium ion with further alkylation of another benzene ring (route 2). For our experiments in the gas phase condition on Beta zeolite, as indicated above, all the propene molecules introduced are consumed after reaction at -80°C . Before elevating the reaction temperature of the capsule, there are therefore mainly remained (unreacted) benzene molecules and produced cumene adsorbed on zeolite. Considering the obtained products and their estimated quantities listed in Table 1, it is clear that the *n*-propylbenzene as primary product is formed via an intermolecular reaction of produced cumene and unreacted benzene. The formation of *n*-propylbenzene is accompanied by

complete scrambling of the carbon atoms in the alkyl chains of cumene and *n*-propylbenzene and by fragmentation towards toluene and ethylbenzene. Toluene, ethylbenzene, *n*-propylbenzene and cumene C- β on H-Beta zeolite are therefore formed on Beta zeolite via the same reaction mechanism on HZSM-11 as proposed by Ivanova et al. [29]. This is in agreement with the second route proposed by Beyer and Borbely [32]. However, the formation of *n*-propylbenzene (C- β and γ) is only observable on the nondealuminated zeolite H-Beta 1. This means that the formation of undesired *n*-propylbenzene can be suppressed on dealuminated H-Beta 3 zeolite.

3.2.2. Catalytic test: conversion and selectivity at various temperatures

All the works on alkylation of benzene by propene on zeolites published in the literature were made at the temperatures higher than 150°C. In the present study, a reaction temperature range of 100–200°C is used. The variation of total conversion and the conversion (of propene) into cumene as a function of reaction temperature are plotted in Fig. 7 for the samples H-Beta 1 and 2 with Si/Al ratios of 10 and 35, respectively. The conversion for the zeolite with Si/Al = 66 is too low and is not shown here. Fig. 8 reports the variation of product selectivi-

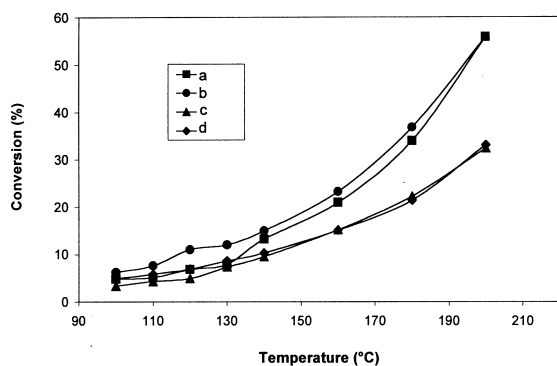


Fig. 7. Variation of total conversion (a, b) and conversion into cumene (c, d) of propene as a function of reaction temperature over H-Beta 1 (a, c) and over H-Beta 2 (b, d) (Bz/prop ratio = 5.0 and WHSV = 7.0 h⁻¹).

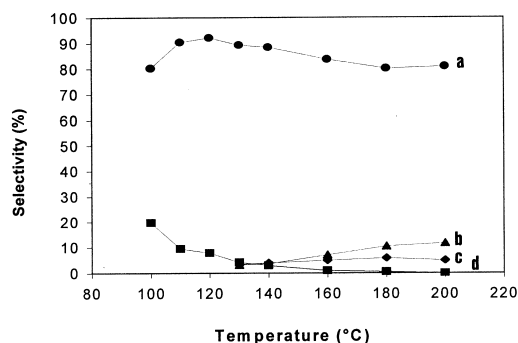


Fig. 8. Variation of product selectivities as a function of reaction temperature over H-Beta 1, cumene (a), 1,3-DIPB (b), 1,4-DIPB (c) and TIPB (d) (reaction conditions: Bz/prop ratio = 5.0 and WHSV = 7.3 h⁻¹).

ties over H-Beta 1 as a function of reaction temperature and Fig. 9 for H-Beta 2. Both experiments were performed with a benzene/propene ratio of 5.0. The total conversion and the conversion into cumene on both H-Beta 1 and 2 zeolites, which are lower than 15%, are very close in the reaction range of 100°C to 140°C. With increasing the reaction temperature, the total conversion and the conversion into cumene increase obviously, and the total conversion becomes higher than the corresponding conversion into cumene. As can be seen, both the total conversion and the conversion into cumene are very similar on two catalysts used in the reaction temperature range studied. Moreover, the formation of by-products in-

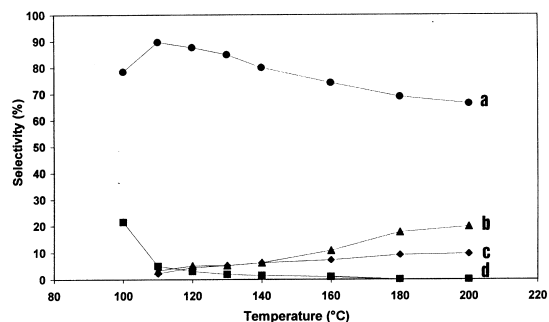


Fig. 9. Variation of product selectivities as a function of reaction temperature over H-Beta 2, cumene (a), 1,3-DIPB (b), 1,4-DIPB (c) and TIPB (d) (reaction conditions: Bz/prop ratio = 5.0 and WHSV = 7.3 h⁻¹).

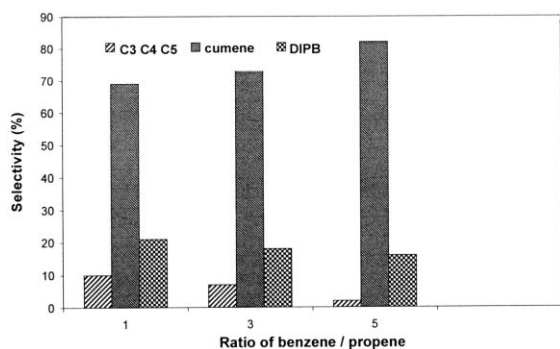


Fig. 10. Selectivities vs. the benzene/propene ratio at 190°C and WSHV = 4 h⁻¹ over H-Beta 1.

creases with increasing reaction temperature (and conversion). Cumene, 1,3-diisopropylbenzene (DIPB) and 1,4-DIPB and 1,3,5-triisopropylbenzene (TIPB) are the main reaction products. Only traces of oligomers and cracking products are observed. The general profile and tendency of the curves are similar for both catalysts. At low temperature (100°C), cumene and TIPB are main products. While at higher temperatures (> 180°C), which are the typical alkylation temperatures used by other researchers [34], cumene and DIPB are main products. The formation of TIPB is quite important at 100°C with about 20% (and 80% of cumene) selectivity, but the amount of this molecule formed decreases quickly with increasing temperature. On the other hand, the production of DIPB increases from 7% at about 120°C to 30% at 200°C for H-Beta 2 and to 15% for H-Beta 1. This suggests that the transalkylation between benzene and TIPB to produce DIPB and cumene occurs mainly at higher temperatures. The production of 1,4-DIPB is found to be half the production of 1,3-DIPB. Moreover, H-Beta 2 leads to a higher formation of DIPB at higher temperature than others.

Another study about the selectivities vs. the ratio of benzene/propene was performed at higher temperature (190°C) for comparison with other works [4,12,37]. When the ratio of benzene/propene increases, the alkylation of ben-

zene is enhanced, while the oligomerization and cracking reaction, which lead to the formation of small alkanes and alkenes, such as C3, C4, C5 and C6, as well as the formation of DIPB, are disfavored (Fig. 10). These results are in agreement with previously reported works [4,26]. Therefore, an excess of benzene is important for optimal alkylation conditions.

3.2.3. Catalyst ageing

Fig. 11 shows the variation of conversion as a function of reaction time at 100°C. The initial conversion (the first point in this figure) which was measured at 5 min after introduction of reactants into microreactor, ranks in an order for the three studied samples as follows: H-Beta 1 > H-Beta 2 > H-Beta 3. However, H-Beta 2 shows a deactivation less important than that of H-Beta 1 and, H-Beta 3 presents a very low conversion at any reaction time. Fig. 12 depicts the variations of product selectivities over H-Beta 1 as a function of reaction time and shows an important decrease of the formation of cumene to a plateau at about 65% and for the DIPBs and the TIPB, an increase in production till plateaus is observed. This indicates thus that DIPBs and TIPB are secondary products. The selectivity of DIPB and that of TIPB are about

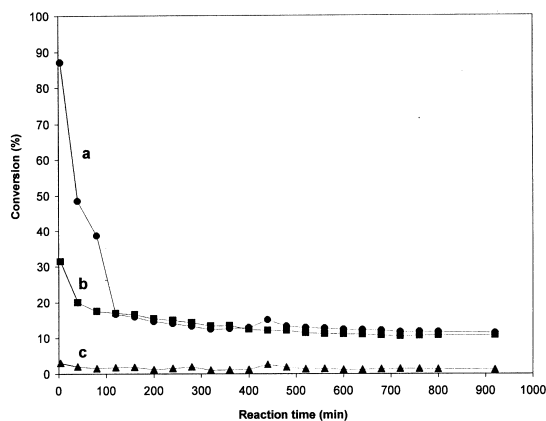


Fig. 11. Variation of products as a function of the time on stream over H-Beta 1 (100 mg of catalyst, reaction temperature: 100°C, Bz/prop ratio = 5.0 and WSHV = 7 h⁻¹), cumene (a), TIPB (b), 1,4-DIPB (c) and 1,3-DIPB (d).

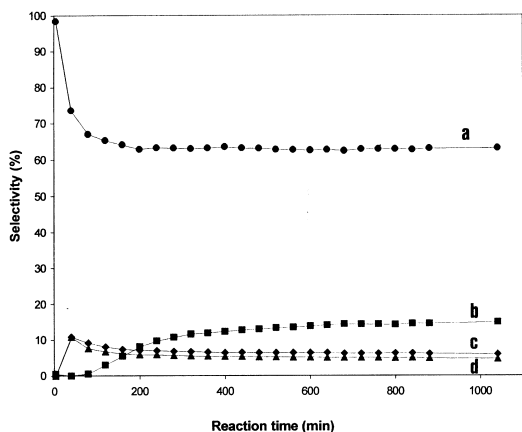


Fig. 12. Ageing study of H-Beta 1 (a), H-Beta 2 (b) and H-Beta 3 (c) with time on stream (100 mg of catalyst, reaction temperature: 100°C, Bz/prop ratio = 5.0 and WSHV = 7 h⁻¹).

10% and DIPBs and TIPB 14%, respectively, in these conditions.

3.2.4. Formation of coke studied by thermal analysis

Cokes are mainly responsible of the deactivation of the catalysts. The coke formation in zeolite has been widely studied [35,36] and depends on the size and shape of the space available near the active sites, diffusion path of the organic molecules in the pores of zeolites. Coke formation can be consecutive or competitive to the reaction leading to the desired product. It was reported that the disproportionation of cumene can be accompanied by dealkylation with formation of propene which transforms rapidly into coke [36]. To better understand the coke formation in the gas phase of alkylation of benzene with propene on Beta zeolite, a thermogravimetric study (in air from 20°C to 800°C with a heating rate of 10°C/min) was made and the species deposited on catalyst during the reaction has been analyzed. Since the H-Beta 1 in the ageing test shows a strong loss in catalytic activity with increasing time on stream, only the formation of coke on this catalyst was studied. Fig. 13 represents the TG of H-Beta 1 after time on stream of 2 h (A), 12 h (B) and 24 h (C). Three distinct weight losses are observed.

The first in the range of 25°C to 190°C is endothermic and corresponds to the desorption of water as explained in the previous section. The second in the range of 190°C to 300°C is also endothermic which could be assigned to the desorption of oligomeric products adsorbed on catalyst according to our previous IR study [26] and that of Haw et al. [27]. Whereas the third in the range of 300°C to 650°C is strong exothermic. This stems very likely from the combustion of the cokes deposited on the catalyst. The assignments of the peaks and corresponding weight losses are reported in Table 2. It can be clearly seen that the weight loss resulting from desorption of water from catalyst decreases ini-

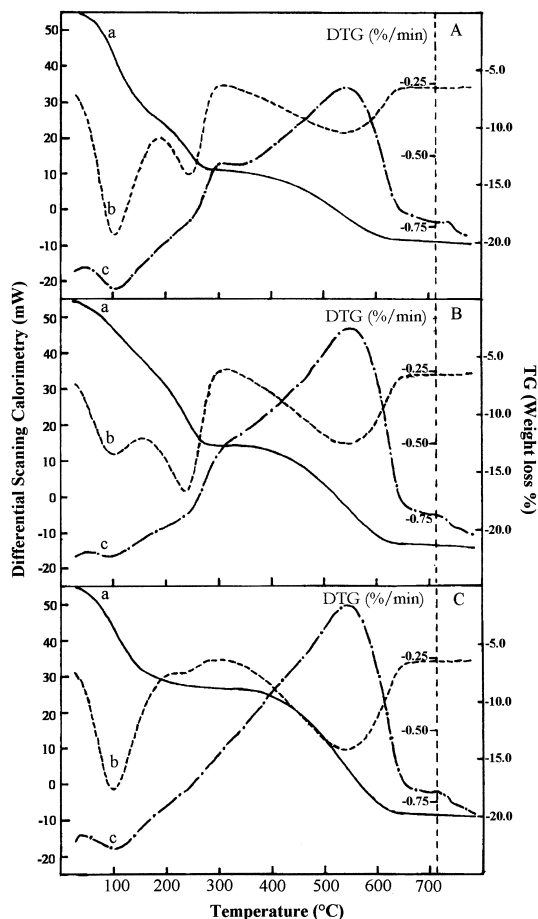


Fig. 13. TG of H-Beta 1 after, respectively, 2 h (A), 12 h (B) and 24 h (C) reaction at 100°C with Bz/prop ratio of 5.0 and WSHV = 7 h⁻¹.

Table 2

Thermogravimetric analysis of coke formation at different reaction time on H-Beta 1 (reaction temperature: 100°C, Bz/prop ratio = 5.0 and WSHV = 7 h⁻¹)

Reaction time (h)	Weight loss (%) at different temperature range (°C)		
	25–190 ^a	190–300 ^b	300–650 ^c
2	9.1	4.5	6.5
12	5.4	7.2	8.9
24	8.4	0.8	10.9

^aDesorption of water.

^bDesorption of oligomers adsorbed on catalyst.

^cCombustion of cokes deposited on catalyst.

tially and then increases and that arising from the desorption of oligomeric products adsorbed by catalyst increases initially and then decreases sharply. These oligomeric products were formed from propene on the basis of our previous IR study [26] and that of Haw et al. [27]. The weight loss due to the combustion in air of cokes deposited on catalyst increases significantly with increasing reaction time. This indicates that more cokes are deposited on catalysts and the coke formation is enhanced as the reaction time increases. Owing to the limit of the void volume of zeolite, these three samples which are withdrawn from reactor after 2, 12 and 24 h reaction respectively, have the similar total weight loss, i.e., the sum of weight losses in three ranges. We should take care of these results when we want to draw some conclusions from the variation of weight losses due to the desorption of water and oligomeric products adsorbed on catalysts since after the withdraw of the catalysts from reactor and before the thermal analysis, the catalyst samples were exposed in atmosphere. Anyway, the sharp decrease in weight loss due to the desorption of oligomeric products and constant increase in weight loss because of combustion of cokes indicate clearly that the oligomeric products adsorbed on catalyst will be transformed to cokes as reaction time increases. It should be pointed out also that after 2 h reaction, there are already 6.5% in weight of cokes deposited on

catalysts and from 2 h to 12 h only 2% in weight of supplementary cokes deposited on catalyst. The sharp decreases in conversion (Fig. 11a) at initial reaction stage should result from the first important deposition of cokes on active sites of catalysts. The supplementary formation of cokes affect only slightly the conversion on catalysts. The coke formation in the gas phase alkylation of benzene by propene comes from the oligomerization of propene and is a consecutive coking as proposed by Guisnet and Magnoux [35]. Our previous IR study [26] and that of Haw et al. [27] confirmed also this coke formation mechanism.

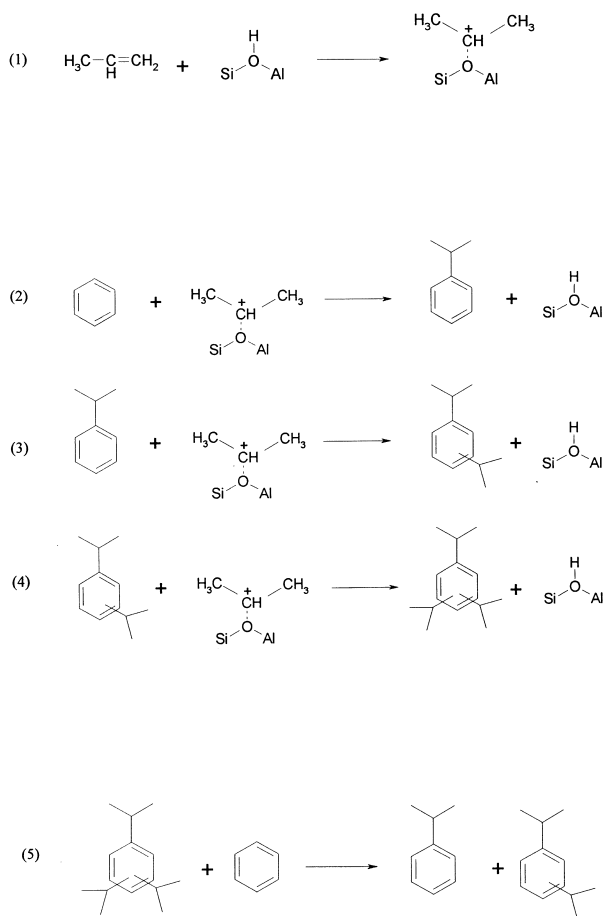
4. Discussion

4.1. Reaction mechanism

From our present work, the more the benzene used, the more the selectivity into cumene is important. It is known that the benzene could only adsorb on positive charged sites in H-Beta zeolites [38]. The isopropyl cations are formed on a protic site. The electrophile attack of the isopropyl cation on the aromatic cycle in interaction with a positively charged site would be disfavored. It also exists a competitive adsorption between benzene and propylene, but our previous results have shown that adsorption of propene on protonated zeolites is much stronger than that of benzene [26]. Thus, the more the ratio benzene/propene is important, the more propene molecules are distant and the less the oligomerization is observed. Moreover, the fact that the selectivities of all the products vary in the same profile as a function of reaction temperature both on H-Beta 1 and 2 zeolites in spite of different amounts of framework Brönsted acid sites present in these two zeolites indicates that isopropyl cations would be formed first on the surface of zeolites and the nucleophile attack of benzene on the isopropyl cations would

then occur. The number of framework Brønsted acid sites can affect only the number of isopropyl cations formed and consequently the conversion, but not the selectivities of products. That is why the conversion is observed to rank in the same order as the Al content in zeolites. The same trend has already reported by Bellussi et al. [15] in liquid phase alkylation of benzene with propene. All these results point out a classical mechanism via carbenium ions but of the type Eley–Rideal as Smirniotis and Ruckenstein [13] have suggested for large pore zeolites. The alkylation of benzene with propene via an electrophilic substitution mechanism on aromatic ring has been claimed by Perego et al. [16] in the liquid phase reaction conditions using Beta, ZSM-12 and Y zeolite as catalyst.

As observed in the catalytic testing study, at low reaction temperatures, only cumene and TIPB are main products while at higher reaction temperatures, the formation of cumene and DIPB predominates. The present results indicate also that both TIPB and DIPB are secondary products and *n*-propylbenzene is not observed at catalytic testing conditions used. Combining the present ^{13}C NMR study, the catalytic testing results and our previous IR observation [26], the alkylation reaction of benzene by propene at low and high reaction temperatures on H-Beta zeolites can be summarized by Scheme 1. The reaction pathways proposed here are very similar to those described by Bellussi et al. [15] although the reaction conditions are quite different.



Scheme 1. Alkylation reaction of benzene by propene on H-Beta zeolites.

4.2. Apparent activation energy

Apparent activation energies were determined after having confirmed that the conversion is a function of the contact time: Conversion = $f(\text{catalyst weight}/\text{reactant flow})$ and then there is no apparent physical diffusion control. The determination of the apparent activation energies was applied for H-Beta 1 and 2 for a temperature range of 100°C to 200°C by using Arrhenius equation [39]. The apparent activation energies of the reaction for H-Beta 1 and 2 are 38 ± 2 and 32 ± 2 kJ/mol, respectively. These energies are obtained for the total reaction, i.e., alkylation, oligomerization and coke formation. The energies for the unique conversion into cumene are 34 ± 2 and 28 ± 2 kJ/mol, respectively. In all the case, the values are between 28 and 38 kJ/mol. If the reaction is totally controlled by the diffusion, the value would be even less than 10 kJ/mol but a chemical process needs generally more than 80 kJ/mol [39]. The values are then quite weak and lower than those found in the literature [6,25] for other zeolites, and when the Si/Al ratio increases, the apparent activation energy decreases further. Therefore, the reaction regime would not be totally chemical and there would be a contribution due to the diffusion of the reactants and products in the channels of zeolite. Perego et al. [16] have studied the possible diffusion limitations of cumene and of three DIPB isomers by computational calculation. In Beta zeolite, cumene diffuses substantially unhindered with an energy barrier quite low of around 20 kJ/mol. The energy barriers decrease in the order *o*-DIPB (212 kJ/mol) > *m*-DIPB (57 kJ/mol) > *p*-DIPB (14 kJ/mol). These computational results did not take the presence of large amount of silanols into account. It is known that the different transport modes of organic molecules can affect the activity and selectivity of reaction, consequently the activation energy of reaction. However, besides this steric effect studied by Perego et al., some other factors, which may be more important, for example, the

interaction of reactant and products with silanols that increases the diffusion barrier of molecules, should be also considered. We think that the diffusion of reactants and products interacting with silanols from one silanol to another plays a more important role in decreasing the apparent activation energy of reaction. The interaction of benzene and propene with silanol groups of H-Beta zeolite has been already reported [19,26,38]. As discussed in the part of characterization of catalysts, it is observed that as H-Beta is further dealuminated, the quantity of silanols increases and that of bridging OH groups decreases. There are actually more silanol groups on the dealuminated zeolite and the acidity of these silanols are found to increase with increasing Si/Al ratio, the interaction of reactants and products with silanols becomes more important. The reaction regime in our present conditions would be therefore neither a real chemical step, nor a pure physical diffusion step. This effect would be particularly important in Beta zeolites which contain more silanols. It is also possible that the physical diffusion described by Perego et al. takes part in also in decreasing the apparent activation energy.

5. Conclusion

By FTIR, it has been shown that H-Beta zeolite is a very active for this reaction with propene but it leads also to fast oligomerization at low temperature. NMR experiments have shown that the reaction of alkylation is already complete at -80°C on these catalysts. Dealuminated H-Beta is less active but form less undesired *n*-propylbenzene and the deactivation is reduced. The high ratio of benzene/propene favors the formation of cumene and disfavors the oligomerization of propene. Tripropylbenzene is formed at lower temperatures and then transformed by transalkylation into DIPB and cumene at higher temperatures ($> 130^\circ\text{C}$). The alkylation of benzene with propene on H-Beta zeolites occurs via an Eley–Rideal-type mecha-

nism. A special diffusion of reactants and products from one silanol group to another in Beta zeolite is evidenced. This kind of transport reduces the apparent activation energy. More work is needed to better understand this transport effect. The thermal analysis reveals a transformation of oligomers to coke during the course of reaction. The coke formation in the gas phase conditions is a consecutive mechanism.

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