

# Linear butene skeletal isomerization over boron-promoted ferrierite

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## Abstract

Boron-promoted potassium-ferrierite catalysts were prepared following the wet impregnation technique. Both boron concentration and pH of impregnating solution were changed. Catalytic behavior was measured during the butene skeletal isomerization.  $H^+$  ion exchange induced by impregnation medium and presence of boron species promote catalytic activity, isobutene yield, and catalyst stability. The catalyst impregnated with 0.01 M solution at pH 0.8 showed the best performance. The effect of temperature, butene partial pressure, and contact time was evaluated. The high stability of this catalyst is an important goal. Large conversion and high isobutene yield were reached in the 400–525 °C range; the largest yield (38%) was obtained at 475 °C. Both linear butene conversion and isobutene yield increased by increasing contact time or by decreasing the butene partial pressure. Isobutene yield remained practically constant during 24 h of reaction. Carbonaceous deposit formed during reaction was characterized by temperature-programmed oxidation and by FTIR. Coke amount at different reaction conditions was lower than 0.7%. Active catalysts displayed the maximum of the combustion peak between 560 and 608 °C, shifting to higher temperature when reaction temperature increases. After 24 h of reaction at 450 °C, the carbonaceous deposit only reaches 0.9%, being it 6.0% after 120 h.

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**Keywords:** Linear butenes; Skeletal isomerization; Isobutene; Boron–potassium ferrierite; Stability

## 1. Introduction

Linear butene skeletal isomerization is an attractive route to produce isobutene, raw material for the synthesis of methyl-*tert*-butyl ether, largely used as an octane booster in reformulated gasolines.

Ferrierite, a zeolite with a structure of bidimensional channels, is one of the materials that present better catalytic behavior in the linear butene isomerization, with a high selectivity to isobutene [1]. Nevertheless, this selectivity is reached after some minutes-on-stream when a carbonaceous deposit is formed, since it suppresses undesirable side reactions [2].

The presence and type of acid sites, their acid strength, the density and their distribution have been evaluated to understand the catalytic performance of ferrierite in the butene isomerization reaction [3]. The characteristic behavior of this zeolite is a high conversion with low isobutene selectivity at a short

time-on-stream, being it associated with the presence of strong acid sites [4].

Ferrierite in the potassic form does not present activity in the butene skeletal isomerization [5]. The acid strength distribution of this catalyst does not show strong acid sites. The addition of tungsten species on the potassium ferrierite promotes the isobutene production even without changing the profile of acid strength distribution [5].

Deactivation processes of acid materials during hydrocarbon transformations have been related to the type of acid sites and to their strength and density [6]. On ferrierite catalysts, Brønsted acid sites have been associated to the isobutene formation while Lewis acid ones to undesirable side reactions [7].

By focusing the catalytic performance, an ideal material should present activity with high selectivity and yield. Ferrierite samples were impregnated or exchanged with tungsten species and their catalytic behaviors were evaluated during the butene isomerization reaction. Samples prepared by exchange reached the best performance, being important the preparation technique on the formation and/or promotion of strong acid sites [8]. Catalytic behavior of ferrierite impregnated with

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boron and platinum species was measured in order to analyze their effect on the active sites [9].

The objective of this work was to study potassium-ferrierite catalysts promoted with boron, prepared by the wet impregnation technique. The effect of boron concentration in the impregnating solution and pH of preparation medium were studied. Catalytic behavior of these materials was measured in the butene isomerization reaction. Product distributions were analyzed to understand the effect of catalyst composition. Carbonaceous deposits formed during the reaction were characterized by temperature-programmed oxidation (TPO) and by Fourier transformed infrared spectroscopy (FTIR).

## 2. Experimental

### 2.1. Catalyst preparation

Ammonium and potassium ferrierites, identified as NH<sub>4</sub>-FER and K-FER, respectively, were supplied by TOSOH, Japan (samples HSZ-720NHA and HSZ-720KOA, respectively). The SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio is 17.8. The crystalline structure was characterized by X-ray diffraction using a Rich-Seifert Iso-DebyeFlex 2002 diffractometer, being the diffraction spectrum range  $3^\circ < 2\theta < 60^\circ$ .

Catalysts were prepared following the wet impregnation technique. K-FER was used as starting material. Boric acid (H<sub>3</sub>BO<sub>3</sub>) was used as boron precursor; solutions with 0.01 and 0.10 M concentrations were employed. Typical preparation conditions were: 11 ml of solution for each gram of solid, and maintaining 6 h at 60 °C with continuous stirring. The pH was modified between 0.8 and 8.0 by adding 0.4 M nitric acid solution. After the impregnation step, samples were filtered and then dried overnight in an oven at 110 °C. Samples were identified as B(*c*-pH)K-FER, being *c*: boron concentration in impregnating solution, and pH: pH of preparation medium. A sample was prepared under similar conditions but without boron addition, being it identified as N(pH)K-FER.

### 2.2. Catalytic behavior

The catalytic behavior during the 1-butene reaction was measured in a continuous down-flow, fixed-bed quartz tubular reactor operated at atmospheric pressure. Catalyst weight varied among 250 and 750 mg, and sieved to 35–80 mesh. Samples were pretreated heating in a nitrogen stream up to 550 °C, keeping this temperature for 30 min. After this pretreatment, NH<sub>4</sub>-FER was transformed into ferrierite in the protonic form, identified as H-FER. Then, samples were cooled to the reaction temperature, which was studied in the 400–525 °C range. B(0.01–0.8)K-FER, N(0.8)K-FER, and H-FER were also evaluated at 300 °C. For reaction, a pure 1-butene stream was co-fed with nitrogen; 1-butene partial pressure was varied between 0.07 and 0.30 atm. B(0.01–0.8)K-FER was also tested under reaction conditions during long time (120 h).

The reactant and reaction products were analyzed by on-line gas chromatography, using a 30 m long, 0.54 mm o.d. GS-Alumina (J&W) megabore column, operated as follows: 5 min

at 100 °C, then heating at 10 °C min<sup>-1</sup> up to 185 °C, keeping this temperature for 30 min. From these data, catalytic activity, isobutene yield, and by-product distribution were calculated on a carbon basis. Catalytic activity is expressed as linear butene conversion, grouping together the three linear butene isomers. It is based on the fact under reaction conditions, the 1- to 2-butene isomerization quickly reaches the equilibrium via double-bond migration.

### 2.3. Characterization of carbonaceous deposits

Carbonaceous deposit formed on catalysts during the butene reaction was characterized by TPO in an equipment designed to enhance both sensibility and resolution [10]. Combustion products were completely converted to methane on a nickel catalyst; methane was continuously analyzed by a flame ionization detector. Experiments were carried out using a 6% oxygen in nitrogen stream (20 ml min<sup>-1</sup>), heating 12 °C min<sup>-1</sup>. Sample weight was 0.01 g. Calibration was periodically checked to verify the CO and CO<sub>2</sub> complete conversion into methane.

The carbonaceous deposit was also characterized by FTIR, using a SHIMADZU 8101M spectrometer. Coked samples were powdered and diluted to 0.5% in potassium bromide (Merck). Then, fine discs were prepared and placed into a cell designed for this characterization. Measurements were made under vacuum and at room temperature.

## 3. Results

### 3.1. Catalytic behavior

The effect of preparation conditions of materials on the catalytic performance during the linear butene skeletal isomerization reaction was studied. Fig. 1 displays butene conversion, selectivity to isobutene, and isobutene yield at 450 °C and 5 min of operation, for samples prepared at different pH and at two concentrations of impregnating solution. By decreasing the preparation pH, butene conversion and isobutene yield increase; the largest values were reached

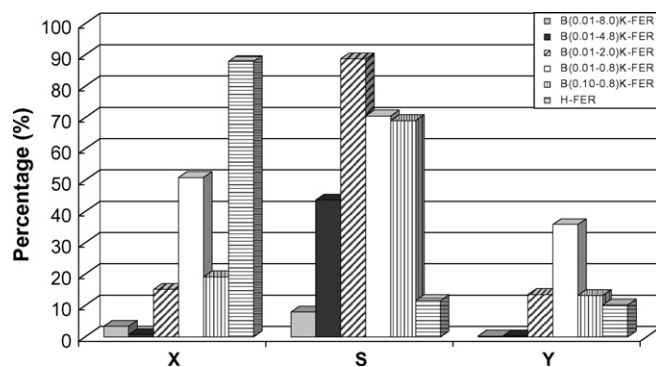


Fig. 1. Linear butene conversion (X), selectivity to isobutene (S), and isobutene yield (Y) for different B-K-FER catalysts. H-FER corresponding values are also included. Reaction conditions: 450 °C, atmospheric pressure, 0.10 atm butene partial pressure, 0.43 h contact time, and 5 min-on-stream.

with the material impregnated in the most acidic medium (pH 0.8). By increasing the concentration of impregnating solution from 0.01 to 0.10 M, butene conversion and isobutene yield decrease. Catalytic behavior remained practically constant as a function of time-on-stream (not shown); stability is an important characteristic of these materials. Catalytic behavior of H-FER, also included in Fig. 1, shows the highest conversion (87.9%) with a very low isobutene selectivity (11.6%), being the isobutene yield only 10.2%. By considering the high influence of the pH during the impregnation, N(0.8)K-FER sample prepared without boron was evaluated. Its catalytic behavior at 300 °C was compared to the B(0.01–0.8)K-FER and H-FER corresponding ones. After 120 min-on-stream, H-FER displays 75.8 and 24.4% decrease in conversion and isobutene yield, respectively. N(0.8)K-FER improves the behavior, only decreasing 25.0% conversion and 5.1% isobutene yield. The best performance is reached with B(0.01–0.8)K-FER decreasing 23% conversion while isobutene yield increases 3.3%. Then, although the impregnation medium induces H<sup>+</sup> ion exchange, the presence of boron improves the catalytic performance of these materials.

According to the previous results, the effect of reaction temperature, contact time and butene partial pressure during the butene isomerization reaction was analyzed using the catalyst prepared at pH 0.8 and impregnated with 0.01 M solution. Results are shown in Table 1. In the reaction temperature range studied, the highest butene conversion is reached at 400 °C (61% at 5 min), but isobutene selectivity and yield present the lowest values. At 425 °C conversion diminishes, increasing both selectivity and yield. At 450 °C, conversion does not change, increasing lightly isobutene yield. Catalytic behavior is practically the same between 450 and 525 °C. The highest isobutene yield is observed at 475 °C (37 and 38% at 5 and 120 min, respectively). Above 425 °C, this catalyst displays a high stability. Contact time was analyzed in the 0.22–0.65 h range. Catalytic behavior at 0.43 h is considered as a reference. By reducing contact time to 0.22 h, conversion significantly decreases while the isobutene yield diminishes and selectivity increases. By increasing contact time to 0.65 h, conversion does

Table 1  
Linear butene conversion (*X*), selectivity to isobutene (*S*), and isobutene yield (*Y*) for B(0.01–0.8)K-FER for different reaction conditions at 5 and 120 min-on-stream

<i>T</i> (°C)	<i>P</i> <sub>C<sub>4</sub></sub> (atm)	W/F (h)	<i>X</i> (%)		<i>S</i> (%)		<i>Y</i> (%)	
			5	120	5	120	5	120
400	0.10	0.43	61	53	44	57	27	31
425	0.10	0.43	51	50	66	67	34	34
450	0.10	0.43	51	47	71	79	36	37
475	0.10	0.43	50	46	74	81	37	38
500	0.10	0.43	50	47	72	80	36	37
525	0.10	0.43	49	46	72	77	35	36
475	0.10	0.22	39	36	87	91	34	33
475	0.10	0.65	49	48	79	81	39	39
475	0.07	0.43	47	45	82	84	38	38
475	0.24	0.43	50	48	67	70	34	34
475	0.30	0.43	53	51	62	67	33	34

not change and isobutene yield lightly increases (39%). Butene conversion increases by increasing the reactant partial pressure while both isobutene selectivity and yield decrease. The high reactivity of the alkene could be associated to this behavior.

Fig. 2 displays by-product distributions corresponding to the butene reaction, obtained with several catalysts under different operating conditions. Reaction temperature and butene partial pressure are indicated between brackets after the catalyst identification. B(0.01–0.8)K-FER(450–0.10) shows propene and pentenes as the main by-products, following ethene and C<sub>8</sub><sup>+</sup> in minor proportion; then, C<sub>4</sub>, C<sub>6</sub>, and C<sub>7</sub> fractions and C<sub>1</sub> appear in decreasing order and quantities below than 2%. By-product distribution obtained allows us to consider the formation of dimers as reaction intermediates. The larger C<sub>3</sub> proportion (mainly propene) as compared to C<sub>5</sub> (mainly pentenes) would suggest the C<sub>5</sub> cracking into C<sub>2</sub> and C<sub>3</sub>. B(0.01–0.8)K-FER(475–0.24) and B(0.10–0.8)K-FER(450–0.10) present a qualitative behavior similar to the previous one. However, there are some small differences such as a decrease of C<sub>8</sub><sup>+</sup> fraction with light increase of C<sub>3</sub> and C<sub>5</sub> ones, and the C<sub>7</sub> absence. B(0.01–4.6)K-FER(450–0.10) shows a different behavior. Ethene, pentanes, ethane, propane, propene, methane, and butanes appear in decreasing order; there are no pentenes and C<sub>6</sub><sup>+</sup> fractions. It was not observed significant changes in distributions as a function of time-on-stream for any sample. By-product distribution varies according to the preparation conditions of material.

### 3.2. Deactivation characterization

TPO characterization of carbonaceous deposit formed on catalysts during the butene reaction shows only one combustion peak. Table 2 displays the coke amount for representative samples under different reaction conditions. In all cases, the carbonaceous deposit is very small, varying between 0.1 and 0.7%. For B(0.01–0.8)K-FER and B(0.01–2.0)K-FER, the maximum of combustion peak appears between 560 and 608 °C, shifting to higher temperature when reaction temperature increases. For B(0.01–4.8)K-FER, the maximum of

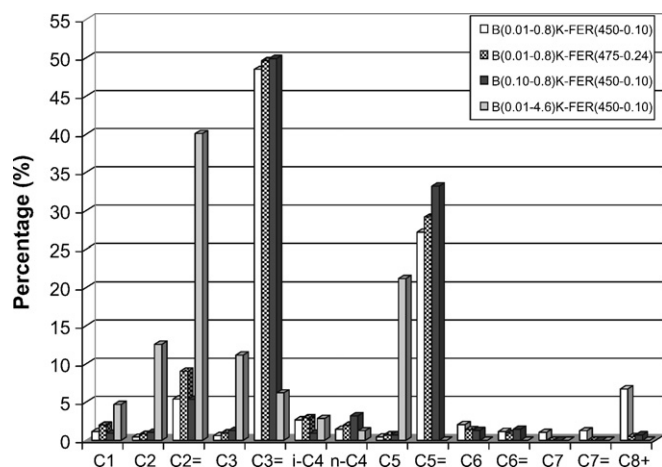


Fig. 2. By-product distribution during the butene isomerization reaction over B-K-FER samples at 0.43 h contact time, and 5 min-on-stream.

Table 2

Amount of carbonaceous deposit formed after 200 min of butene reaction and temperature of the maximum of combustion peak by different catalysts

Catalyst	$T_{\text{reaction}}$ (°C)	Carbonaceous deposit (%)	Temperature of the maximum of combustion peak (°C)
B(0.01–0.8)K-FER	400	0.3	560
	450	0.4	570
	475	0.3	578
	500	0.6	588
	525	0.7	608
B(0.01–2.0)K-FER	450	0.2	602
B(0.01–4.8)K-FER	450	0.1	285

Reaction conditions: butene partial pressure = 0.10 atm; W/F = 0.43 h.

combustion peak appears at lower temperature (285 °C). This could be related to the irreversible adsorption of alkene species on the active sites.

Fig. 3 shows butene conversion ( $X$ ), isobutene yield ( $Y$ ), and isobutene selectivity ( $S$ ) as a function of time-on-stream for B(0.01–0.8)K-FER during 24 h of operation. Along this time,  $X$ ,  $S$ , and  $Y$  only change 8, 14, and 3%, respectively; showing the high stability of the material. It is important to mention that B-K-FER catalysts do not show the high activity with a low isobutene selectivity at a short time-on-stream, which is the characteristic behavior of H-FER, as has been previously reported [2,3,11]. Furthermore, the amount of carbonaceous deposit after 24 h on stream still remains low, being 0.9%. The corresponding TPO profile displays the main combustion peak at high temperature, with its maximum centered at 600 °C, also appearing a shoulder at 340 °C, as shown in Fig. 4. A long-time run showed deactivation of B(0.01–0.8)K-FER, decreasing significantly both conversion and isobutene production, and reaching a carbon content of 6% after 120 h-on-stream.

Preliminary results of FTIR characterization show bands at 3622 and 3467  $\text{cm}^{-1}$  in the  $\text{OH}^-$  characteristic region and bands at 1640 and 1365  $\text{cm}^{-1}$  assigned to olefinics species, for B(0.01–0.8)K-FER(525–0.10). The same bands appear on B(0.01–8.0)K-FER(450–0.10). For B(0.01–0.8)K-FER(450–

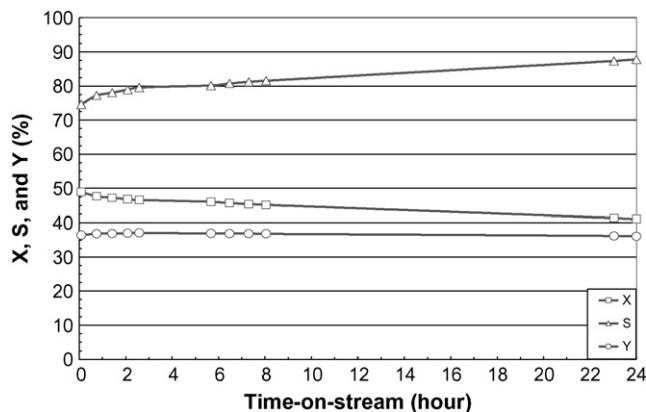


Fig. 3. Linear butene conversion ( $X$ ), selectivity to isobutene ( $S$ ), and isobutene yield ( $Y$ ) for B(0.01–0.8)K-FER as a function of time-on-stream. Reaction conditions: 450 °C, atmospheric pressure, 0.10 atm butene partial pressure, and 0.43 h contact time.

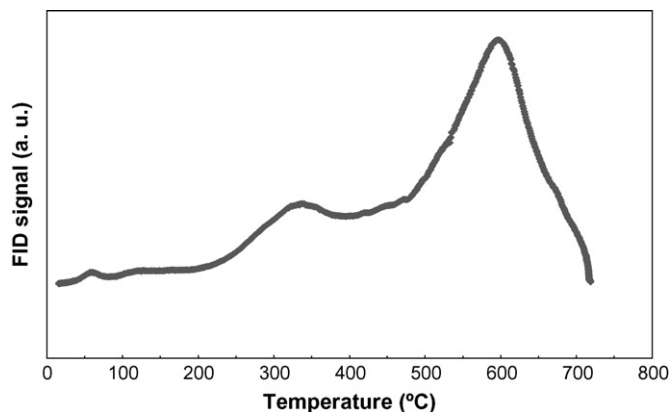


Fig. 4. TPO profile of B(0.01–0.8)K-FER coked during 24 h at 450 °C, atmospheric pressure, 0.10 atm butene partial pressure, and 0.43 h contact time.

0.10) after 24 h of reaction, the intensity of the 3460  $\text{cm}^{-1}$  band decreases and a band at 1520  $\text{cm}^{-1}$  appears, being it related to aromatic species. Previous results with H-FER indicated the 3609  $\text{cm}^{-1}$  band in the  $\text{OH}^-$  stretching region can be shifted to 3649  $\text{cm}^{-1}$ ; this band is associated to bonding  $\text{OH}^-$  which corresponds to Brønsted acid sites.

#### 4. Discussion

Potassium ferrierite does not show activity in the butene skeletal isomerization [11]. The wet impregnation of boron species on this material produces an active, selective and stable catalyst for the isobutene production. Although the impregnation medium induces  $\text{H}^+$  ion exchange, the presence of boron improves the catalytic performance. Previous results showed that the impregnation of tungsten species on K-FER also promotes both activity and isobutene yield [5,11]. Using silica promoted with cations, such as W, it was found that acidity and cation reducibility determine both activity and selectivity during the butene skeletal isomerization reaction [12]. Tungstic acid and ammonium metatungstate used as W precursor on K-FER showed that the presence of W does not significantly modify the profiles of ammonia temperature-programmed desorption, keeping the acidity amount and the acid strength distribution of the unpromoted material [5]. However, in addition to acidity and acid strength distribution, the type of acid sites may also have influence on the catalytic behavior [13]. Tungsten impregnation on alumina promotes the butene skeletal isomerization without modifying the acidity profile of the unpromoted material. This catalytic behavior is explained by considering a Lewis to Brønsted acid sites change [14]. Brønsted acid sites have been considered essential for butene skeletal isomerization through an alkoxide intermediate [12]. Isobutene formation on ferrierite has been related to the concentration of Brønsted acid sites while the Lewis acid sites favor side reactions such as butene dimerization and oligomerization [7]. In another catalytic system, impregnating boron on alumina, it was proposed that strong Brønsted acid sites generated by  $\text{BO}_4$  species present on the surface, are responsible of the linear butene skeletal isomerization [15]. On this catalyst, the presence of weak Brønsted acid sites was

reported under wet conditions [16], while Lewis acid sites were detected in dry conditions [17]. Then, the promotion of catalytic activity and mainly the isobutene yield and the catalytic stability reached with our catalyst could be related to the acid sites formation by  $H^+$  ion exchange and their modification by boron species favoring the presence of Brønsted acid sites, responsible of the skeletal isomerization.

B-K-FER catalysts display practically constant levels of linear butene conversion, isobutene selectivity, and isobutene yield with time-on-stream, indicating a high stability. It is a significant difference compared to the H-FER's characteristic behavior, which presents a high conversion with low isobutene selectivity at a short time, decreasing quickly the activity and increasing isobutene selectivity as a function of time. Similar behavior was obtained with samples prepared by ion exchange, using K-FER as starting material and 0.1–0.5–1.0–1.5 M ammonium nitrate solutions. This behavior has been related to the strong acid sites present on the surface of H-FER, which favor undesirable side reactions, such as oligomerization and cracking, decreasing the isobutene selectivity [4]. On B-K-FER samples the absence of a high activity with low isobutene selectivity at a short time and the high stability displayed by these samples allow us to consider that the active acid sites induced by both  $H^+$  ion exchange and boron have not a strong acid strength and therefore, unfavored side reactions.

The catalytic behavior of any material can be affected by the environment of active acid sites and its density, and also by the restriction imposed by the carbonaceous deposit formed in the pores during the butene reaction [18]. Working with H-FER, the carbonaceous deposit formed under different reaction conditions varied between 7 and 9% [19–21], being the largest proportion of deposit formed during the first minutes-on-stream (i.e. 6.1% carbonaceous deposit after 30 min under reaction conditions) [4]. Recent published results obtained on H-FER with different Si/Al ratios presented 1.8% of coke after 3 h at 350 °C using a H-FER sample with a 19 Si/Al ratio [22]. The catalytic behavior did not significantly change by increasing the Si/Al ratio to 32. According to our results with B-K-FER that has a similar Si/Al ratio (17.8) but operating at 450 °C, the coke amount was only 0.4 and 0.9% after 200 min and 24 h, respectively. Although preliminary analysis detected the presence of Al in the solution obtained after filtering at the end of catalyst preparation and a possible dealuminization should be considered, the behavior should not be significantly changed. The small carbonaceous deposits even operating at a higher temperature, indicate the absence of strong acid sites, which are related to undesirable side reactions and to coke formation. Then, the low levels of carbonaceous deposit formed on B-K-FER samples allow us to consider only a minor effect of that deposit on the catalytic behavior. Nevertheless, after 120 h-on-stream the carbonaceous deposit is 6%. It indicates that the catalyst is capable to form coke content similar to H-FER but in a much longer time. Then, characterization of the type of acid sites and location of boron species are necessary to understand the catalytic performance of these materials. For example, the low coke formation at the beginning of the reaction, and the increase thereafter might be related to the location of boron

species. Initially, the boron species might be blocking the pore mouths, and therefore the available catalytic surface is lower and correspondingly, the coke formation rate is low. During the reaction, the mobility of the boron species might open the pore mouths, and the coke amount keeps increasing continuously. The lower conversion obtained with the catalyst with the higher boron content (0.10 M impregnating solution) may also be explained by the pore-mouth plugging mechanism.

The reaction scheme of linear butene skeletal isomerization on H-FER still remains under discussion. On fresh FER, an unselective material, it has been proposed that the reaction occurs through a bimolecular mechanism [23] or by a monomolecular one [19,24] being the by-products formed on different sites [24]. It has also been reported that an isobutene fraction is formed by a bimolecular mechanism with the by-products [25]. By considering the multimolecular mechanism, firstly butene and isobutene produce oligomers, which then crack to obtain the products [26]. On aged FER, a selective material, it has been proposed that the bimolecular mechanism cannot occur, taking place a monomolecular one [23,24,27]. A pseudomonomolecular mechanism has also been considered to explain the FER catalytic behavior [28]. More recently, it has been suggested that FER channels can work like nanoreactors [29]. Previous works with fresh ferrierite show propene and pentenes as the main by-products [30]. In decreasing order, the by-products obtained during the butene isomerization reaction are propene, pentenes, *n*-butane, octenes, heptenes, hexenes, propane, ethane, and isobutane [21]. The by-product distributions corresponding to B(0.01–0.8)K-FER and B(0.10–0.8)K-FER show propene and pentenes as the main ones, while the  $C_1$  and  $C_2$  amounts are small. It allows us to consider the formation of dimers and/or oligomers as reaction intermediates, which then crack to the other products. Propene proportion is larger than the pentene one; considering that both of them come from  $C_8$  cracking, then a fraction of pentenes could give  $C_2$  plus  $C_3$ . B-K-FER prepared at the highest pH shows ethene and pentanes as the main by-products. It suggests that the by-product distribution is strongly influenced by the catalyst preparation conditions.

## 5. Conclusions

The catalytic behavior of boron-promoted potassium-ferrierite samples during the linear butene skeletal isomerization is strongly influenced by the preparation conditions of these materials.  $H^+$  ion exchange induced by impregnation medium and presence of boron species promote catalytic activity, isobutene yield and catalyst stability respect to K-FER which is inactive in that skeletal isomerization reaction. B(0.01–0.8)K-FER sample displays the best performance, being its high stability a remarkable characteristic. In the temperature range studied, linear butene conversion and isobutene yield reach 46–51 and 34–38%, respectively, between 425 and 525 °C. The largest isobutene production (38%) is achieved at 475 °C. By increasing contact time or by decreasing butene partial pressure, both butene conversion and isobutene yield increase.

The carbonaceous deposit formed during the butene reaction over the B-K-FER catalysts under different reaction conditions is low, less than 0.7%. TPO profiles show only one combustion peak, appearing differences in the temperature of the maximum of this peak. Catalyst impregnated at the highest pH, which presents a low activity, displays the maximum at 285 °C. B-K-FER samples that present catalytic activity show the maximum of combustion peak between 560 and 608 °C. The higher the reaction temperature, the higher the temperature of the maximum of combustion peak. After 24 h of reaction, isobutene production remains stable, decreasing butene conversion while isobutene selectivity increases; the carbonaceous deposit formed after this reaction time is only 0.9%. Nevertheless, this material should be even improved because it deactivates after 120 h-on-stream, increasing coke content up to 6.0%.

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