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Skeletal Isomerization of Linear Butenes on Boron Promoted Ferrierite: Effect of the Catalyst Preparation Technique

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Abstract Potassium and acid ferrierites were impregnated with boron species by wet and incipient wetness techniques. All samples display a medium-intensity band at 3,450–3,470 cm^{-1} associated to Si−OH···O groups corresponding to boron-containing units. The 1,398–1,404 cm^{-1} band assigned to the B–O stretching in BO_3 units does not appear on boron–potassium–ferrierite prepared by wet impregnation. Catalytic performance during the linear butene skeletal isomerization was measured. At 300 °C, boron impregnated by incipient wetness technique on acid ferrierite reduces both linear butene conversion at a short time and isobutene yield in all time range. Boron–potassium–ferrierite prepared by wet impregnation has a suitable acidity to promote isobutene production. At 450 °C, this sample shows the best performance, being the isobutene yield 1.7 times higher than the acid-ferrierite one and reaching the highest isobutene selectivity (92%). This performance is maintained with time. Both isobutene yield and by-product distribution are strongly affected by temperature; dimer intermediates are formed. Finally, both kinds of hydroxyl groups corresponding to 3,466 and 3,635 cm^{-1} bands influence the isobutene production whereas BO_3 sites are inactive for this reaction.

Keywords Boron–ferrierite · Isobutene · Skeletal isomerization · Wet impregnation

1 Introduction

The skeletal isomerization of linear butenes is an alternative route for the production of isobutene, which is used for the methyl *tert*-butil ether synthesis, the poliisobutene production, and in alkylation reactions. The skeletal isomerization reaction takes place on acid catalysts and demands a stronger acidity than the double bond isomerization, but a strong acidity also favors undesirable side reactions such as dimerization–oligomerization, cracking, disproportion, and hydrogen transfer. In order to improve the isobutene selectivity, an ideal skeletal isomerization catalyst should have an adequate acidity strong enough for the isomerization reaction but not too strong for undesirable side reactions.

Ferrierite, a zeolite with a bidimensional pore structure of ten-membered rings (4.2 × 5.4 Å) intersected by eight-membered rings (3.5 × 4.8 Å), shows one of the best catalytic performances during the skeletal isomerization of linear butenes [1]. The characteristic behavior of this zeolite is a high activity with low isobutene selectivity at a short time-on-stream; then, conversion decreases and selectivity increases after some minutes under reaction conditions [1, 2]. This behavior has been related to the type of acid sites [3], the space around the acid site [4], the acid site density [5], and the carbonaceous deposit formation [2, 6]. Among several catalysts, Li- and Cs-exchanged ferrierite was evaluated to investigate the effect of the presence of acid sites on the external surface, the acid site density, and the space around the site over the isobutene selectivity [4]. Catalytic properties of ferrierite exchanged with alkaline earth metals during the linear butene skeletal isomerization were reported [7]. ZSM-5 and ZSM-11 were synthesized with different contents of aluminum and boron, suggesting there are synergistic effects between framework boron and aluminum to enhance the butene skeletal

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isomerization activity [8]. These authors also concluded the acidity of aluminum zeolites can be weakened by incorporating boron into the framework.

Catalytic improvement of both potassium and ammonium ferrierites by tungsten species impregnation, following the incipient wetness technique and using both tungstic acid and ammonium metatungstate as tungsten precursors, was previously reported [9]. Tungsten species on ammonium ferrierite improve catalytic behavior without modifying the acidity profile corresponding to the non-impregnated material, whereas those species on potassium ferrierite promotes catalytic activity but without reaching a high conversion at a short time-on-stream [10]. Tungsten–ferrierite catalysts prepared either by incipient wetness impregnation or by ion exchange were evaluated during the linear butene isomerization reaction in order to study the influence of preparation technique over the catalytic performance [11]. The exchanged samples reach a larger isobutene yield than the impregnated ones. Nevertheless, tungsten-exchanged potassium ferrierite samples display the high activity with a low isobutene selectivity at a short time. A catalyst showing a good isobutene yield with a high isobutene selectivity at a short time-on-stream would be a goal.

The effect of preparation technique of boron–ferrierite catalysts over their behavior during the linear butene skeletal isomerization was studied. Catalysts were prepared by impregnation following both wet and incipient wetness techniques. Potassium and ammonium ferrierites were used as starting materials. Characterization by temperature-programmed reduction (TPR) and infrared spectrometry (FTIR) and the catalytic test of 1-butene reaction at temperatures between 300 and 550 °C and at atmospheric pressure were made in order to explain material behavior.

2 Experimental

2.1 Catalyst Preparation

Ammonium and potassium ferrierites, identified as NH_4-FER and K-FER, respectively, were provided by TOSOH, Japan (samples HSZ-720NHA and HSZ-720KOA, respectively). The SiO_2/Al_2O_3 molar ratio was 17.8. NH_4-FER has Na_2O and K_2O concentrations below 0.05 and 0.10%, respectively.

Catalysts were prepared by both incipient-wetness and wet impregnation. Boric acid (Cicarelli) was used as boron precursor. Solutions with the desirable boron concentration were prepared. K-FER and H-FER (ferrierite in the protonic form obtained by calcining NH_4-FER at 550 °C) were impregnated by the incipient-wetness technique, maintained at room temperature for 4 h, and then dried overnight in an oven at 110 °C. Boron loadings were 0.9 and 1.1 wt.% on K-FER and H-FER, respectively. These samples were identified as B/K-FER and B/FER, respectively. K-FER and NH_4-FER were used as starting materials for wet impregnation. Typical conditions were: a solid-liquid ratio of 1 g:11 mL, 60 °C, and continuous stirring during 6 h. Then, materials were filtered and dried overnight in an oven at 110 °C. These samples were identified as B-K-FER and B-FER, respectively.

Two samples of boron alumina were also prepared by wet impregnation. γ-Al_2O_3 (Azko Nobel, CK-300, 199 $m^2\ g^{-1}$, 0.51 $cm^3\ g^{-1}$) was used as starting material, being impregnating conditions the same ones mentioned above. Boron concentrations used were 0.10 and 0.01 M.

2.2 Catalyst Characterization

The crystalline structure was characterized by X-ray diffraction using a Rich-Seifert Iso-Debyeflex 2002 diffractometer, being the diffraction spectrum range $5 < 2\theta < 60°$ [10].

The surface species reducibility was determined by TPR using an Ohkura TP 2002S equipped with a thermal conductivity detector. Samples were pretreated in situ in a nitrogen stream (60 mL min^{-1}), heating at 9.6 °C min^{-1} and holding 30 min at 550 °C. Then, samples were cooled to room temperature in an argon stream, and finally heated up to 950 °C at 10 °C min^{-1} in 1.8% hydrogen in argon stream.

Ammonia temperature-programmed desorption (NH_3-TPD) measurements were carried out to characterize both total acidity and acid strength distribution of catalysts. Samples were pretreated in situ under the same conditions mentioned above. Then, they were cooled in a nitrogen stream. Ammonia was fed through a sample valve over the bed at 100 °C, followed by a purge with nitrogen at 200 °C during 120 min. Finally, temperature was raised at 10 °C min^{-1} in a nitrogen stream. The ammonia desorption was continuously measured using a thermal conductivity detector.

Catalysts were also characterized by FTIR, using a SHIMADZU 8101M spectrometer. Samples were powdered and diluted to 2% in potassium bromide (Merck). Then, fine discs were prepared and placed into a cell designed for this characterization. Some measurements at room temperature were made injecting butene into the cell, through a sampling valve. These experiments with and without catalyst were made under vacuum.

2.3 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, using 500 mg of catalyst sieved to 35–80 mesh. All samples were pretreated as follows: heating up to 550 °C in a nitrogen stream, keeping this temperature for 30 min; then, they were cooled to desirable temperature. For reaction, a pure 1-butene stream was co-fed with nitrogen at 0.15 atm. 1-butene partial pressure; the temperature range varied from 300 to 550 °C.

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, heating up to 185 °C at 10 °C min^{-1}, keeping this temperature for 22 min. From these data, catalytic activity, isobutene selectivity, isobutene yield, and by-product distribution were calculated on a carbon basis. The catalytic activity is expressed as linear butene conversion, grouping together the three linear butene isomers. It is based on the fact that, under reaction conditions, the 1- to 2-butene isomerization quickly reaches the equilibrium via double-bond migration. Isobutene selectivity is the ratio between isobutene and all reaction products excluding the three linear butenes.

3 Results and Discussion

3.1 Catalyst Characterization

Previous TPR characterization of NH_4-FER and K-FER did not show any peak [10]. Figure 1 displays TPR profiles corresponding to the impregnated materials. B/K-FER and B/FER do not practically show any peak. Both calcined and uncalcined samples display similar profiles which are the same ones that the non-impregnated materials. Profiles corresponding to samples prepared following the wet impregnation present differences, as shown in Fig. 1. B-FER displays the main peak centered at 870 °C, appearing some shoulders. B-K-FER shows a small hydrogen consumption above 300 °C, which is higher from 700 °C.

Figure 2 shows NH_3-TPD profiles. H-FER displays two well-defined peaks, centered at about 305 and 650 °C, assigned to weak and strong acid sites, respectively. It qualitatively agrees with results previously reported [2]. K-FER only shows a peak centered at 350 °C which corresponds to weak acid sites. Boron impregnation on both H-FER and K-FER does not significantly modify the acid strength distribution of the corresponding non-impregnated material. Nevertheless, B impregnated on H-FER by incipient wetness technique reduces both desorption peaks.

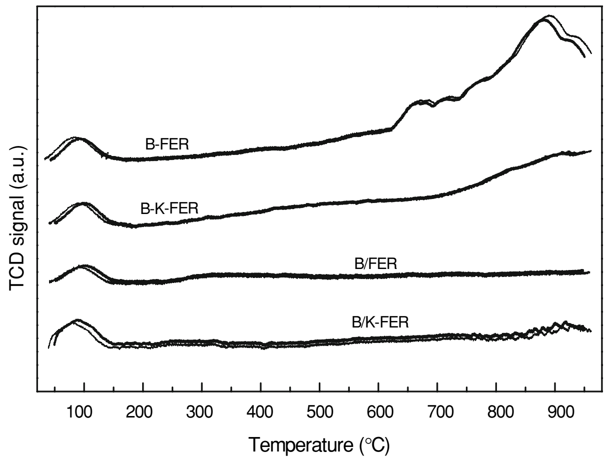


Fig. 1 TPR profiles of boron–ferrierite samples impregnated by both incipient wetness and wet techniques

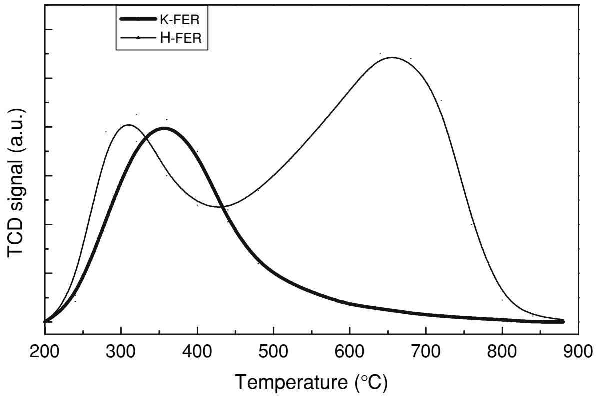
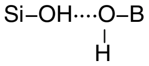


Fig. 2 NH_3-TPD profiles of H-FER (thin line) and K-FER (gross line)

Table 1 shows FTIR characterization of representative samples. By comparing with H-FER, catalysts prepared by the incipient wetness impregnation show a new band at 1,398–1,404 cm^{-1}, having a medium intensity for B/FER and a weak one for B/K-FER. This band is characteristic of the antisymmetric stretching vibrations of B–O in BO_3 units [12]. Another difference is the increase of the 3,450–3,470 cm^{-1} band which corresponds to Si–OH···O groups. This kind of hydroxyl group with the corresponding one to the 3,670 cm^{-1} band are fragments of  $\text{Si–OH}\cdots\underset{\text{H}}{\underset{|}{\text{O}}}\text{–B}$ units [13]. For B/K-FER, the band above 3,600 cm^{-1} is weak and shifts at a lower wave number (3,617 cm^{-1}). B-FER, sample prepared by wet impregnation, displays a similar pattern than B/FER; the only difference is the weak intensity of the 1,398 cm^{-1} band. B-K-FER does not have the 1,404 cm^{-1} band and the 3,466 and 3,635 cm^{-1} bands have medium and weak intensity, respectively. Then, surface species on samples prepared by incipient wetness or wet impregnation show some differences.

3.2 Catalytic Performance

Figure 3a–c show linear butene conversion (Fig. 3a), selectivity to isobutene (Fig. 3b), and isobutene yield

Table 1 Bands (wavenumber values in cm^{-1}) observed in the 1,000–4,000 cm^{-1} region of IR spectra on representative samples and their assignments

H-FER	B/FER	B/K-FER	B-FER	B-K-FER	Assignment
1,020 s	1,070 vs	1,070 vs	1,075 vs	1,070 vs	
1,225 vs	1,234 s	1,234 s	1,234 s	1,234 s	
	1,398 m	1,404 w	1,398 w		1,380–1,404: stretching B–O in BO_3 units
1,640 m	1,650 m	1,640 m	1,636 m	1,650 m	
3,500 w	3,450 m	3,466 m	3,490 m	3,466 m	3,450: O···H–O–Si groups
3,640 m	3,650 m	3,617 w	3,650 m	3,633 w	3,609/3,640: OH associated to Si–Al ions/OH in supercage
					3,670: B–OH
3,750 vw	3,735 vw	3,730 vw	3,735 vw	3,730 vw	3,700–3,720: Si–OH···B groups

vs: very strong; s: strong; m:medium; w: weak; vw: very weak

(Fig. 3c) like a function of time-on-stream at different reaction temperatures for catalysts prepared by incipient wetness and wet impregnation. The performance of H-FER at 300 °C is taken as a reference. B/K-FER does not practically display activity and isobutene is not formed at 300 °C, only taking place the double bond isomerization which is not observed in Fig. 3a because the linear butenes are grouped together as indicated in Sect. 2. The same behavior is obtained with K-FER [9]. At 300 °C, B/FER reaches a 47% conversion after 5 min of reaction, decreasing activity at a long time; the isobutene yield practically remains constant at 4%, being lower than the H-FER corresponding one. At a short time, B/FER reaches a conversion lower than the high one obtained with H-FER (90.2%), whereas at a long time it is similar for both catalysts. At 450 °C and a short time, linear butene conversion even is lower than the corresponding one to H-FER, whereas at a long time it is larger. The isobutene yield increases up to 14%, being similar to the one obtained with H-FER. By considering the performance of catalysts prepared by wet impregnation, B-FER has a qualitative behavior similar to H-FER when reaction takes place at 300 °C. At a short time the same high activity is practically reached, whereas at a long time both conversion and isobutene yield are higher than the H-FER corresponding ones. At 450 °C and a short time, conversion is 82% remaining high even at a long time. Isobutene yield is lower than the one produced at 300 °C. Working with B-K-FER at 300 °C, butene conversion and isobutene yield reach 10 and 6%, respectively, and practically remain constant with time. Reaction temperature has a strong influence on the isobutene yield. When reaction takes place at 450 °C, increasing activity up to 26%, the isobutene yield is practically 3.8 times higher than the one obtained at 300 °C, being also higher than the H-FER corresponding one, and similar to the one produced by B-FER. B-K-FER also reaches the highest isobutene selectivity (92%), keeping constant with time. At 550 °C, the linear butene conversion is higher than the one obtained at 450 °C but decreases with time; the isobutene yield strongly decreases with time-on-stream, being 2.7 times lower than the one obtained at 450 °C after 160 min.

Comparing samples prepared by incipient wetness impregnation with H-FER, the effect of boron on H-FER produces a strong decrease in both activity at a short time and isobutene yield. On H-FER, the high activity at a short time associated to a large by-product formation, was related to strong acid sites present on the surface [14]. Moreover, Lewis acid sites on H-FER enhance oligomerization and cracking reactions [15]. These side reactions have been suppressed by removing the non-selective acid sites using acid treatment [16, 17]. Acidic properties of Mg-ZSM-22 were modified by impregnating with boric acid [18]. Boron mainly poisoned the strong acid sites, resulting to a decrease in side reactions and an increase in the isobutene selectivity. It partially agrees with the behavior observed: B/FER does not show the high activity at a short time-on-stream. Nevertheless, a decrease in the isobutene production is also observed. Then, it can be considered boron impregnated by the incipient wetness technique on H-FER modifies both strong and medium acid sites which are active for the by-product formation and responsible to the isobutene production, respectively. The incipient-wetness impregnation technique requires the use of solutions with high concentrations. The formation of polyborates from boron concentrated solutions has been reported [19]. Then, it allows to consider the blockage of channels of ferrierite by boron species reducing the specific surface area and consequently the active sites exposed.

By considering samples prepared by wet impregnation, B-FER shows a similar qualitative performance than H-FER improving both butene conversion and isobutene yield but showing the same high activity at a short time. It can be understood considering the low concentration of boron used for the wet impregnation which unfavors the formation of polyborates, allowing the diffusion of boron

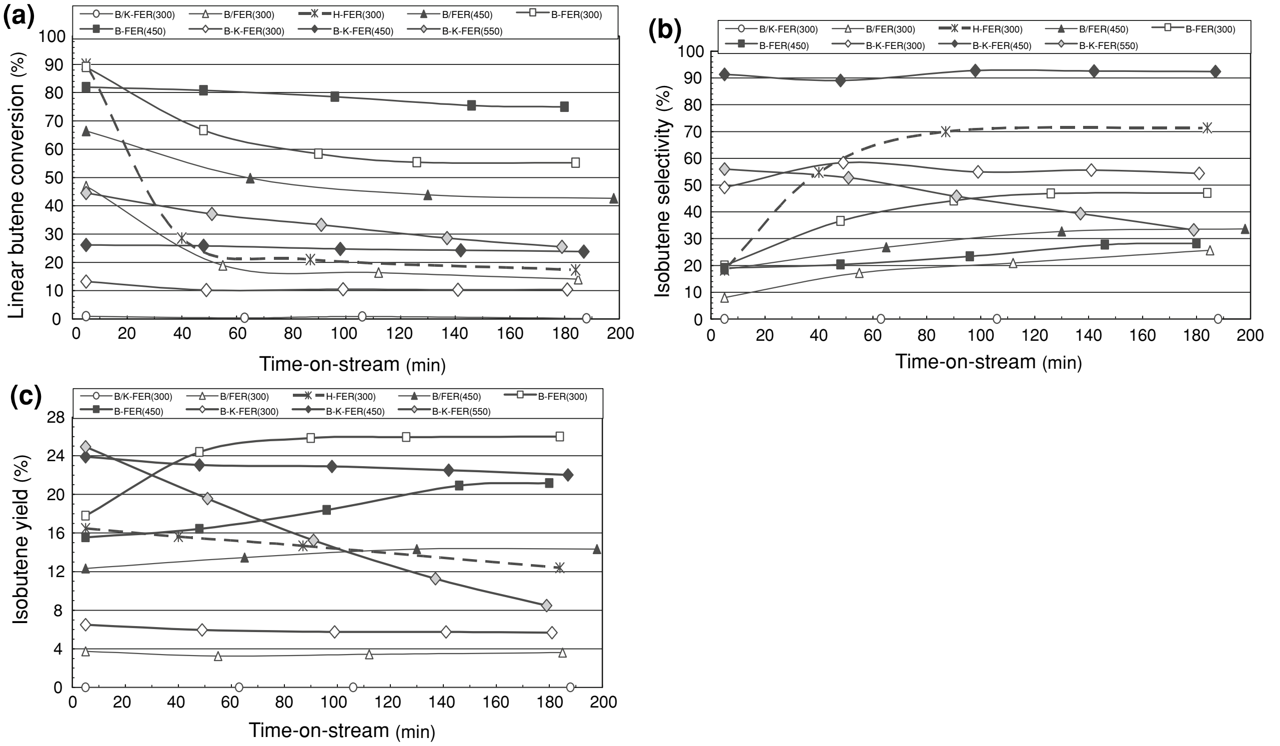


Fig. 3 (**a**) Linear butene conversion, (**b**) selectivity to isobutene, and (**c**) isobutene yield as a function of time-on-stream during the 1-butene skeletal isomerization on samples impregnated by incipient wetness (thin line) and wet (gross line) techniques. Activity test at 300 °C (open symbol), 450 °C (black symbol), and 550 °C (gray symbol), 1 atm. and 0.15 atm. 1-butene partial pressure. *Note*: H-FER at 300 °C (⋇), included as a reference

species in all channels. Boron species on the K-FER surface improve activity comparing with K-FER which is inactive. Independent of reaction temperature, B-K-FER does not show the high activity at a short time indicating the absence of strong acid sites. It agrees with the NH_3-TPD results which show that K-FER samples only display the low-temperature desorption peak. At 450 °C, B-K-FER practically produces an isobutene yield of 1.7 times higher than the H-FER one and also reaching the highest isobutene selectivity (92%). Furthermore, this performance is maintained with time-on-stream. A similar behavior was reported using CoAlPO-11 molecular sieve [20]. The presence of boron into the framework of ZSM-5 and ZSM-11 reduces acidity and enhances the isobutene selectivity [8]. $BO_4^=$ species on the alumina surface generate strong Brønsted acid sites [21]. These acid sites were associated to the isobutene selectivity [2, 15]. In this way, two samples of boron-alumina prepared by wet impregnation were evaluated al 450 °C, reaching butene conversions of 25.2–27.8% and isobutene yields of 20.7–23.3% after 5 min-on-stream. These results suggest boron on K-FER promotes active sites having a suitable acidity capable to enhance the linear butene skeletal isomerization.

Table 2 shows the isobutene yield at two times-on-stream for boron-impregnated ferrierites, H-FER, a tungsten-exchanged potassium ferrierite sample (W-K-FER), and a boron-alumina sample at 300 °C and/or 450 °C. The best performance is reached with B-K-FER at 450 °C, being the same one obtained with W-K-FER at 300 °C. Nevertheless, this tungsten containing sample displays the high activity with a low isobutene selectivity at a short time [11]. B-Al_2O_3 also reaches a high isobutene yield (22.8%) at 5 min on reaction; thus, indicating boron promotes a suitable acidity to produce isobutene. Nevertheless, this catalyst show a 12% decrease in isobutene yield after 120 min-on-stream. By considering FTIR characterization (Table 1), B/K-FER shows the 1,404 cm^{-1} band assigned to BO_3 units and two bands in the OH region, at 3,466 and 3,617 cm^{-1} having medium and weak intensity, respectively. This catalyst is inactive for the isobutene production; then, BO_3 sites are inactive. At 300 °C, B-FER reaches a higher performance than H-FER; the 3,640–3,650 cm^{-1} band shows a medium intensity for both materials whereas the 3,470 cm^{-1} band has a medium intensity on B-FER and a weak one on H-FER. By comparing B-K-FER and H-FER, both samples show similar bands, differences appear in the intensity and a minor shifting of them. H-FER displays a weak 3,500 cm^{-1} band and a medium 3,640 cm^{-1} one. B-K-FER shows a medium 3,466 cm^{-1} band and a weak 3,650 cm^{-1} one. The 3,466 cm^{-1} band

Table 2 Isobutene yield for boron-containing samples impregnated by both incipient wetness and wet techniques at two times-on-stream and at different reaction temperature

	B-K-FER	B-FER		H-FER	B/FER	B/K-FER	B-Al_2O_3	W-K-FER[a]
T (°C)	450	300	450	300	450	300	450	300
5 min	24.0	17.6	15.5	15.5	12.0	0	22.8	24.0
140 min	23.5	25.5	21.0	13.5	14.5	0	20.6	26.5

[a] Reference [11]

has been assigned to groups associated to acid sites which are active for the isobutene production. Nevertheless, B/K-FER is inactive even though displaying this band. Then, the 3,650 cm^{-1} band is also necessary. This band has a medium intensity on H-FER, reaching this catalyst a high activity with a low isobutene selectivity at a short time. This behavior has been related to strong acid sites [14]. On B-K-FER, the 3,635 cm^{-1} band has a weak intensity and this catalyst shows a high isobutene selectivity in all time range. Then, the intensity of that band could be associated to the amount of strong acid sites. Additional temperature-programmed oxidation analysis show 6.9, 4.5, and 0.3% of carbonaceous deposit formed on H-FER, B/FER, and B-K-FER respectively. The absence of strong acid sites favors the desorption of products before the adsorption of reactants and/or reaction intermediates and their transformation into coke. Acid strength of active sites has a strong influence over the amount of the carbonaceous deposit formed during the butene reaction. Carbon content diminishing could be related to the weak intensity of the 3,635 cm^{-1} band on B-K-FER and the medium intensity of the 3,450 cm^{-1} one on B/FER. Finally, it allows to consider an active material for isobutene production needs both 3,466 and 3,635 cm^{-1} bands, whereas the amount of carbonaceous deposits and the isobutene selectivity at a short time would be related to the intensity of the 3,635 cm^{-1} one.

3.3 By-product Analysis—Reaction Scheme

Figure 4a, b display by-product distribution for samples prepared by wet impregnation and at different reaction temperatures. At 5 min (Fig. 4a), H-FER and B-FER show the same distribution after reaction at 300 °C. The largest by-product proportion corresponds to pentenes (24.5%), following propane and butane in similar proportions (15.0%), and then propene and hexenes, being the other fractions lower than 10%. The practically negligible C_1 and C_2 proportions and the appearing of C_6 and C_7 fractions allow to consider the formation of dimers and trimers or oligomers. After reaction at 450 °C, distribution changes: the largest proportion corresponds to propene (41.5%), increasing ethene (18.5%), decreasing significantly pentenes and butane, and disappearing hexenes. It could be considered the cracking of dimers/oligomers by effect of the higher reaction temperature. B-K-FER at 300 °C shows a particular behavior, the main by-products are the C_8^+ fraction (28.5%), propene (27.5%), and pentenes (26.0%). This by-product distribution indicates dimer intermediates are still formed. It could consider desorption of intermediates are not favored at 300 °C. When reaction takes place at 450 °C, the C_8^+ fraction does not appear and propene reaches the largest proportion (45.0%), following pentenes (29.5%) and ethene (11.1%). The C_8^+ fraction diminishing and the high isobutene selectivity (Fig. 3b) and isobutene yield (Fig. 3c) allow consider the bimolecular mechanism takes place and isobutene is formed through it. At 550 °C, propene (33.5%) and methane (29.1%) are the main by-products, following ethene (12.5%) and pentanes (8.7%) whereas the other fractions are lower than 5%. At a long time-on-stream (Fig. 4b), by-product distributions are qualitatively similar. H-FER and B-FER at 300 °C show an increase in propene, decreasing propane and butane while the C_8^+ fraction only increases for B-FER. At 450 °C, B-K-FER shows a light decrease in propene and an increase in pentenes.

The reaction mechanism during the linear butene isomerization on ferrierite remains under discussion. On the fresh ferrierite, a non-selective material, the reaction occurs through either a bimolecular mechanism [22] or a monomolecular one [6, 23], being the by-products formed on different active sites [23]. A substantial amount of isobutene formed via a non-selective bimolecular mechanism together with by-products was reported [20]. On the aged catalyst, considered as a selective material, the bimolecular mechanism cannot occur whereas the monomolecular one can take place [22, 23]. A pseudo-monomolecular mechanism was also reported in order to explain the catalytic behavior of ferrierite [24]. An exhaustive analysis of the linear butene skeletal isomerization, including the possible reaction schemes and the locations of active sites, has been published [25]. More recently, the H-FER pore system has been considered as equivalent to a series of non-interconnected nanoreactors into which linear butene selectively isomerizes through an autocatalytic process [26]. By-product distributions

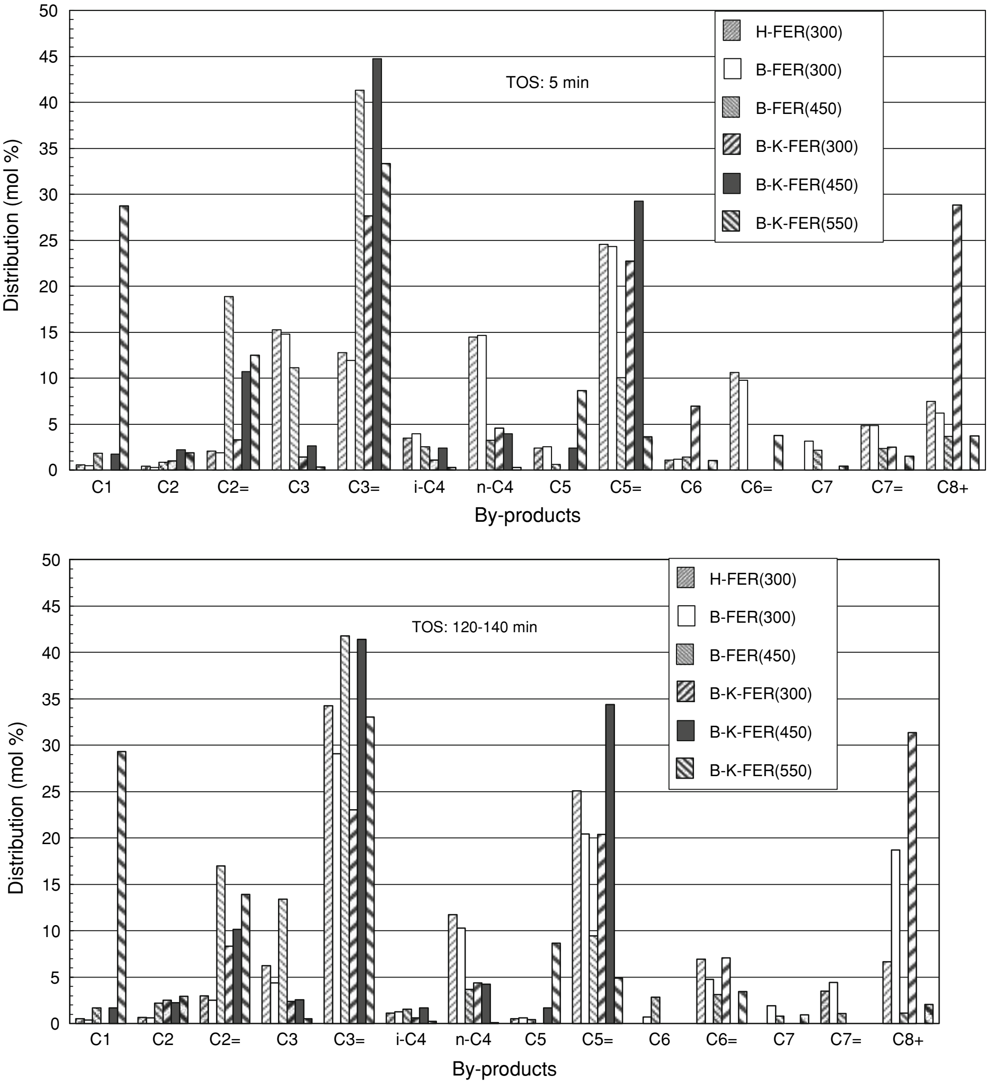


Fig. 4 By-product distribution (mol %) during the 1-butene reaction on samples prepared by wet impregnation, at 5 min (**a**) and 120–140 min (**b**). Activity test at 300, 450, and 550 °C, 1 atm., and 0.15 atm. 1-butene partial pressure

obtained in the 300–550 °C range suggest that the bimolecular mechanism still takes place at a long time. At 300 °C, the main by-product is the C_8^+ fraction, being conversion and isobutene yield only 10 and 6%, respectively. It would indicate that cracking-desorption of reaction intermediates is unfavored. It agrees with previous results which stated the irreversible adsorption of butene on ferrierite below 350 °C [22]. At 450 °C, the absence of C_8^+, the higher isobutene yield, and the higher stability suggest desorption of reaction products, including isobutene, is favored by cracking of dimers, reaction intermediates, or oligomers. The highest reaction temperature (550 °C) favors hydrogenolisis reaction, being propene and methane the main by-products, even though the presence of $C_6^=$, $C_7^=$, and C_8^+ fractions indicates the oligomer formation still takes place. B-Al_2O_3 samples having suitable acidity for the isobutene production show propene and pentenes as the main by-products and a decrease in stability. The presence of $C_6^=$, $C_7^=$, and C_8^+ fractions as by-products for ferrierite samples could be related to the pore structure and the residence time of reactant and reaction products into the pores, favoring successive reactions. It can be understood by considering the pseudo-monomolecular scheme above mentioned [24]. Moreover, the pore structure of ferrierite could also influence the location and the type of carbonaceous deposit formed, affecting stability. Finally, isobutene production is strongly influenced by temperature and by the strength of active acid sites or the type of them whereas by-product distribution and catalyst stability should be related to pore structure.

4 Conclusions

K-FER, NH_4-FER, and H-FER were impregnated with boron species following both wet and incipient wetness techniques. By FTIR characterization, all samples display a medium-intensity band at 3,450–3,470 cm^{-1} which is associated to Si–OH···O groups corresponding to boron-containing units. The 1,398–1,404 cm^{-1} band assigned to the antisymmetric stretching vibrations of B-O in BO_3 units does not appear on B-K-FER. On this catalyst, the 3,466 and 3,635 cm^{-1} bands have medium and weak intensity, respectively.

For catalysts prepared by incipient wetness impregnation, isobutene is not formed on B/K-FER at 300 °C. This sample shows the 1,398–1,404 cm^{-1} band corresponding to BO_3 units; then, BO_3 sites are inactive for the isobutene production. B/FER does not show the high activity at a short time-on-stream but the isobutene production also decreases. Then, all active acid sites could be affected during catalyst preparation by incipient wetness impregnation.

For catalysts prepared by wet impregnation, B-FER displays a qualitative behavior similar to H-FER, improving both linear butene conversion and isobutene yield but showing the high activity with a low isobutene selectivity at a short time. B-K-FER maintains its performance with time-on-stream showing the best catalytic stability, without the high activity at a short time. At 450 °C, the isobutene yield is practically 1.7 times higher than the H-FER one and also reaching the highest isobutene selectivity (92%). Then, boron on K-FER promotes active sites with a suitable acidity, being selective to the isobutene production. The main by-products at 300 °C are the C_8^+ fraction, propene, and pentenes, suggesting dimer intermediates are formed. At 550 °C, the presence of methane and propene like main by-products can be explained by considering hydrogenolisis reactions favored by the high temperature. Finally, both kinds of hydroxyl groups corresponding to 3,466 and 3,635 cm^{-1} bands are necessary to give an active material for the isobutene production.

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