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Skeletal isomerization of linear butenes on ferrierite: Effect of the presence of lower olefins in the feed and of operating conditions

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The skeletal isomerization of linear butene on ferrierite, at atmospheric pressure and 0.15 atm 1-butene partial pressure, was studied by feeding 1-butene streams with different ethene and propene concentrations and exploring several operating conditions. At short time-on-stream (5 min), the strongest acid sites govern the catalytic behavior, independent of the operating conditions in the studied ranges. At longer times, the reaction temperature mainly defines the conversion level. The higher the temperature, the larger the linear butene conversion. Temperature also has a strong influence over the nature of the carbonaceous deposit formed during reaction. At 400 °C, the deposit mainly shows an aromatic nature. The presence of lower olefins as impurities in the feed modifies both catalytic activity and by-product distribution. By decreasing the ethene concentration, the C_5^+ fraction in the product stream increases and a lower carbonaceous deposit is formed. Using a nitrogen stream saturated with water during both pretreatment and reaction, the catalytic activity increases and the coke amount slightly diminishes, but the isobutene production is unfavored.

KEY WORDS: skeletal isomerization; isobutene; ferrierite; feed impurities; coke

1. Introduction

The skeletal isomerization of linear butenes has gained importance as an alternative route for the production of isobutene, which is used for the methyl *tert*-butyl ether synthesis and in alkylation reactions. That skeletal isomerization reaction takes place on acid catalysts. The ferrierite zeolite shows one of the best catalytic behaviors, as reported by numerous articles in the literature [1–4].

The effect of operating conditions over catalytic behavior of ferrierite during the skeletal isomerization of linear butene has been reported [5,6]. Nevertheless, topics related to ferrierite deactivation have constituted the main focus of interest, especially in order to understand the isobutene selectivity improvement with time-on-stream. This characteristic catalytic behavior of ferrierite has been related to the carbonaceous deposit formation [3,7], to the type of acid sites [5], to the space around the acid site [8], and more recently to the acid site density [9].

The inner pores of ferrierite have been modified by plasma-polymerized propylene in order to identify the role of carbonaceous deposit during the skeletal isomerization of linear butenes [7]. Nevertheless, there are no available data related to the effect of lower olefins present in the butene feed either on catalytic behavior of ferrierite or on its deactivation.

In this paper, we study the effect of the presence of ethene and propene, as impurities of the feed, over both catalytic behavior and deactivation of ferrierite during the skeletal isomerization of linear butene. The ethene concentration in the butene feed is modified by passing the stream through a molecular sieve bed placed before the isomerization reactor. The effect of both the temperature and the presence of water under reaction conditions is also analyzed.

2. Experimental

An ammonium ferrierite sample was provided by TOSOH, Japan (sample HSZ-720NHA). The SiO_2/Al_2O_3 molar ratio was 17.8, Na_2O and K_2O concentrations being below 0.05% and 0.10%, respectively. The crystalline structure was characterized by X-ray diffraction using a Rich-Seifert Iso-Debyeflex 2002 diffractometer, the diffraction spectrum range being $0 < 2\theta < 60\,^\circ$.

The catalytic behavior during 1-butene isomerization was studied in a continuous down-flow, fixed-bed quartz tubular reactor operated at atmospheric pressure, using 500 mg of catalyst sieved to 35–80 mesh. Samples were heated in a nitrogen stream at $17.3\,^\circ\mathrm{C\,min^{-1}}$ from 25 to 550 °C, keeping this temperature for 30 min, thus obtaining samples in the acid form. After heating, samples were cooled to the selected temperature in the nitrogen stream. For catalytic tests, a pure 1-butene stream was co-fed with nitrogen, 0.15 atm 1-butene partial pressure. In order to modify the ethene concentration in the butene

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Table 1
Composition of different 1-butene feeds

1-C_4^{2-} suppliers	Matheson [a]	AGA			PLP
		Original feed [b]	Passing through a 4 Å molecular sieve		
			4 h at 200 °C [c]	6 h at 300 °C [c]	
C_2	n.d.	0.04	0.03	0.04	0.01
C_2^{2-}	**0.01**	**0.15**	0.12	**0.03**	**0.03**
C_3	0.03	0.04	0.04	0.05	0.01
C_3^{2-}	**0.01**	**0**	**0**	**0**	**0**
n-C_4	0.06	0.04	0.04	0.04	0.05
1-C_4^{2-}	99.89	99.73	99.77	99.84	99.90

n.d.: not detected.

[a] Feed identified as p^+.

[b] Feed identified as e^+.

[c] Activating conditions of the molecular sieve bed.

stream, some experiments were made passing the feed through a 4 Å molecular sieve bed placed before the reactor. Table 1 shows the composition of the different butene streams fed. Experiments either starting the reactant feed at a low catalytic bed temperature (100 or 200 °C) and then increasing it up to reaction temperature (300 or 400 °C, respectively) or saturating the nitrogen stream with water (0.08 atm water partial pressure) used in both pretreatment and reaction steps, were carried out. 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 at 10 °C min^{-1} up to 160 °C, keeping this temperature for 60 min. From these data, catalytic activity, isobutene yield, and 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 operating conditions, the 1-butene to 2-butene isomerization quickly reaches the equilibrium via double-bond migration.

The carbonaceous deposit formed during reaction was characterized by temperature-programmed oxidation in an apparatus specially designed to improve sensitivity and resolution [10]. Combustion products were completely converted to methane on a nickel catalyst, methane being continuously analyzed by a flame ionization detector. Experiments were carried out using a 6% oxygen in nitrogen stream (20 ml min^{-1}), heating at 12 °C min^{-1}. The sample weight was about 0.01 g. Calibration was periodically checked to verify the complete conversion of carbon monoxide and carbon dioxide into methane.

3. Results

Figure 1 shows linear butene conversion (A) and isobutene yield (B) as a function of time-on-stream at 300 and 400 °C, feeding 1-butene streams with different amounts of ethene or propene and saturating the nitrogen stream with water in some experiments. At short times (5 min) a high activity is reached, practically independent of reaction temperature in the used range, being only slightly higher when the water-saturated nitrogen stream is fed. At 300 °C, the characteristic behavior of ferrierite is observed: a high conversion with low isobutene selectivity at short times, quickly diminishing the activity and improving that selectivity. Ethene-containing feed reaches a higher conversion than when propene is present. The highest conversion is obtained by feeding the water-saturated nitrogen stream, while isobutene yield increases more slightly with time-on-stream. At 400 °C and long times, activity is higher than the one reached at 300 °C. Practically no difference is observed between the butene feeds containing ethene or propene, while an activity increase and a lower isobutene yield are shown when using the water-saturated nitrogen stream.

Figure 2 shows by-product distributions corresponding to different conditions, at 5 min (A) and 135 min (B). Differences appear according to temperature, time-on-stream and feed. At 400 °C, C_3 (propane plus propene) and C_5^+ (mainly C_5 olefins) fractions are the main by-products. At 5 min, the C_5^+ fraction is practically two times the C_3 one for the propene-containing feed while both fractions are similar for the ethene-containing feed (with the nitrogen stream saturated or unsaturated with water). At 135 min, propene shows a slight increment and the C_5^+ fraction increases 10% when the feed contains propene and almost 50% for the ethene-containing feed, while other by-products decrease. At 300 °C, the main by-product is the C_5^+ fraction. At 5 min, this fraction reaches between 70% and 76%, being 10% higher for the ethene-containing feed (with the nitrogen stream saturated or unsaturated with water). n-Butane, propane and propene follow in proportion. At 135 min, the C_5^+ fraction remains as the main by-product, increasing 15%

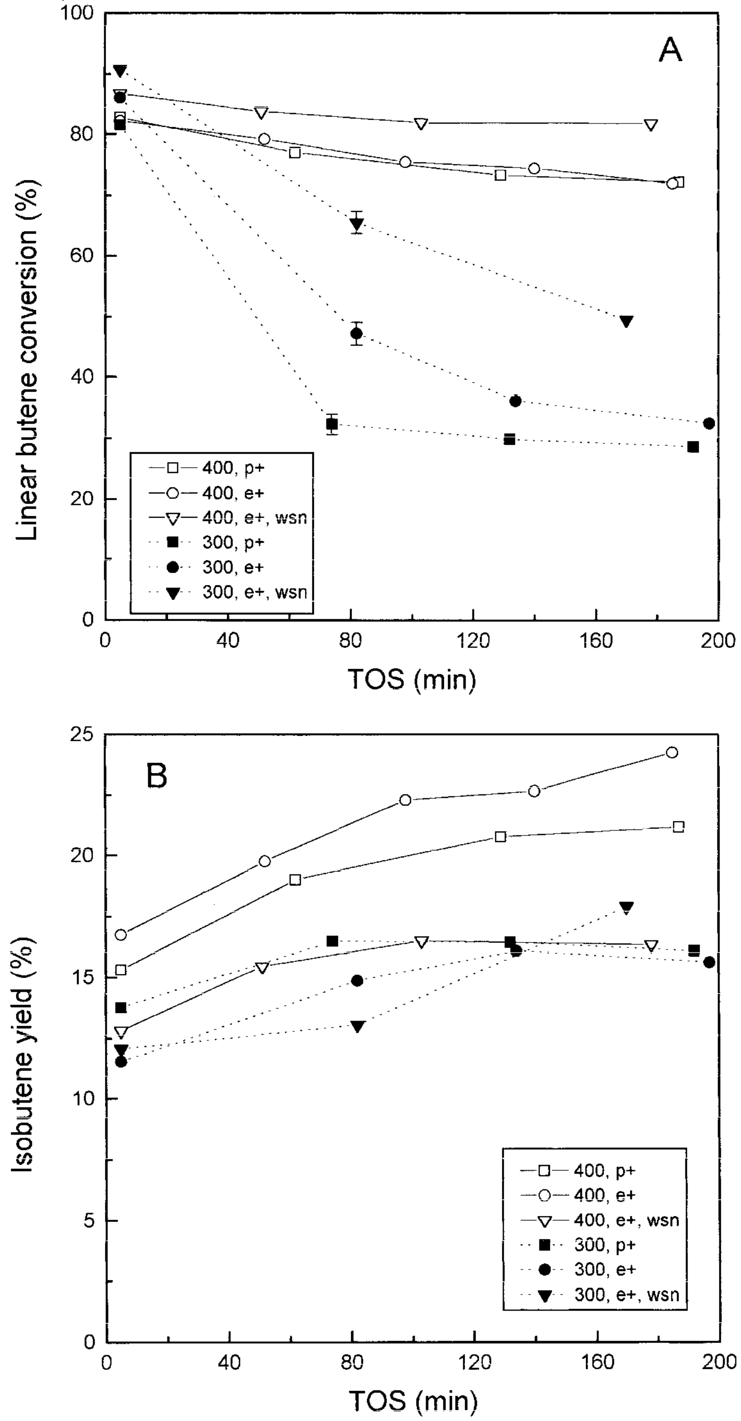

Figure 1. (A) Linear butene conversion and (B) isobutene yield as a function of time-on-stream during the 1-butene skeletal isomerization on ferrierite at 300 °C (dashed line and filled symbols) and 400 °C (solid line and open symbols), feeding 1-butene streams with ethene (○, e^+) or propene (□, p^+) as impurities and saturating the nitrogen stream with water (▽,wsn).

for the water-saturated nitrogen stream. Propene increases practically two times while other by-products decrease.

Figure 3 displays the catalytic performance at 400 °C, feeding the 1-butene stream through a 4 Å molecular sieve bed placed before the isomerization reactor. The molecular sieve was activated either at 200 °C for 4 h or at 300 °C for 6 h. The more severe the activating conditions, the lower the ethene amount remaining in the butene feed, practically reaching the concentration corresponding to a 1-butene feed used as co-polymer. By decreasing ethene concentration in the butene stream fed, conversion increases and isobutene yield diminishes. Moreover, by-product distribution at 5 min shows a 35% propene decrease while the C_5^+ fraction increases, slightly diminishing the other by-products (also displayed in figure 2). At 135 min, neither propane

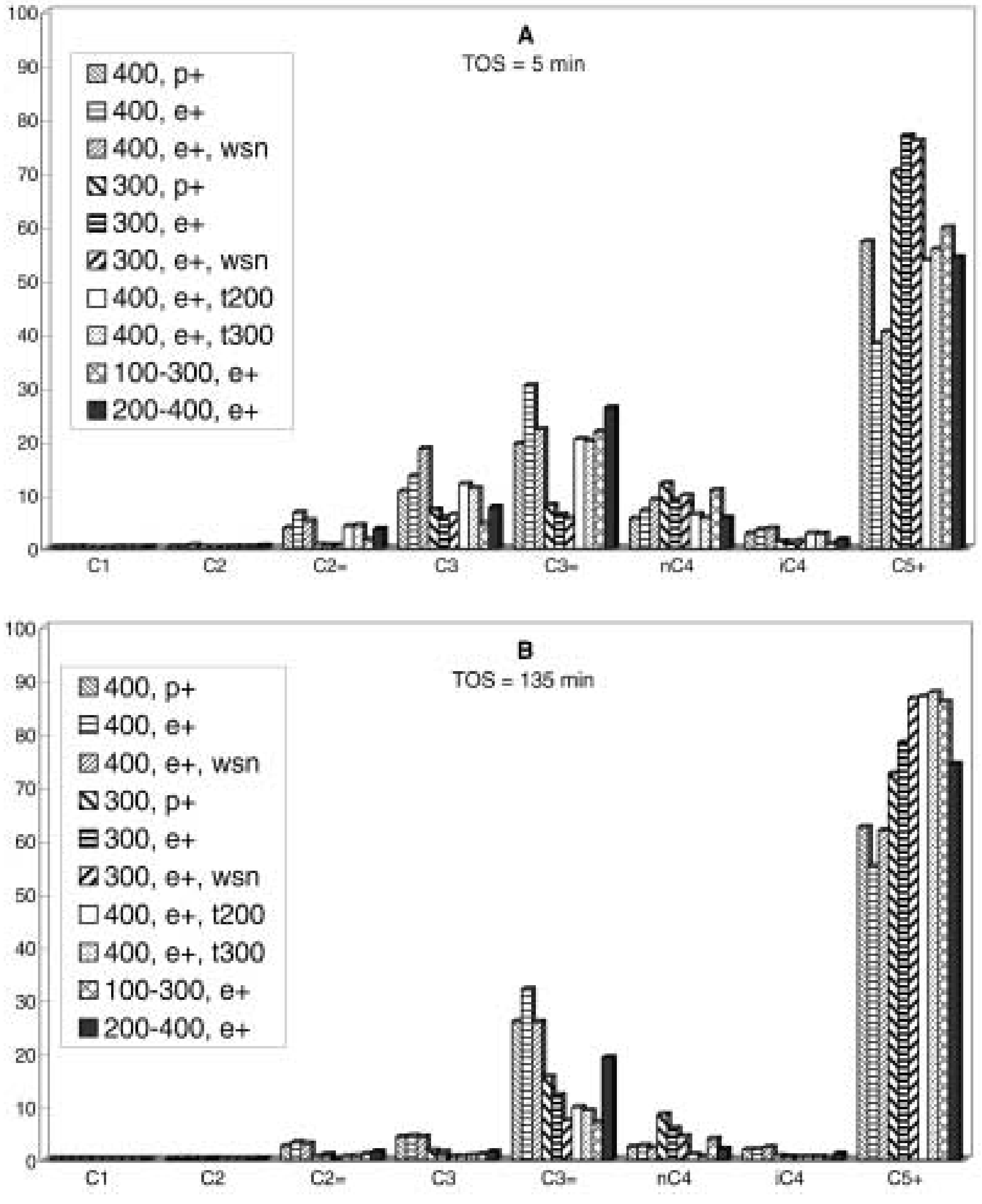

Figure 2. By-product distributions at 5 min (A) and 135 min (B) corresponding to the 1-butene reaction on ferrierite at atmospheric pressure and 0.15 atm 1-butene partial pressure. Samples identified according to figures 1 and 3.

nor butane are present, propene decreases four times its proportion, and the C_5^+ fraction increases significantly.

Figures 4 and 5 display temperature-programmed oxidation profiles of carbonaceous deposit formed under different conditions, including the corresponding carbon content. Two characteristic patterns are shown. Profiles corresponding to reaction at 300 °C (figure 4) present two well-defined combustion peaks and a smooth one between them, carbon contents remaining below 7%. These samples present a light brown color at the end of catalytic test. After reaction at 400 °C, oxidation profiles (figure 5) show only the high-temperature combustion peak, carbon contents being larger than 7%. After the isomerization reaction, these catalysts appear completely black. For each reaction temperature, carbon content is lower with the water-saturated nitrogen stream, being slightly higher for the propene-containing feed. At 400 °C, the lowest amount of carbonaceous deposit is formed when the feed is passed through the molecular sieve bed.

Finally, experiments starting the butene feed over the catalyst bed at low temperature and then increasing it up to the reaction one were made. This operating form allows one to diminish the high activity at short time-on-stream,

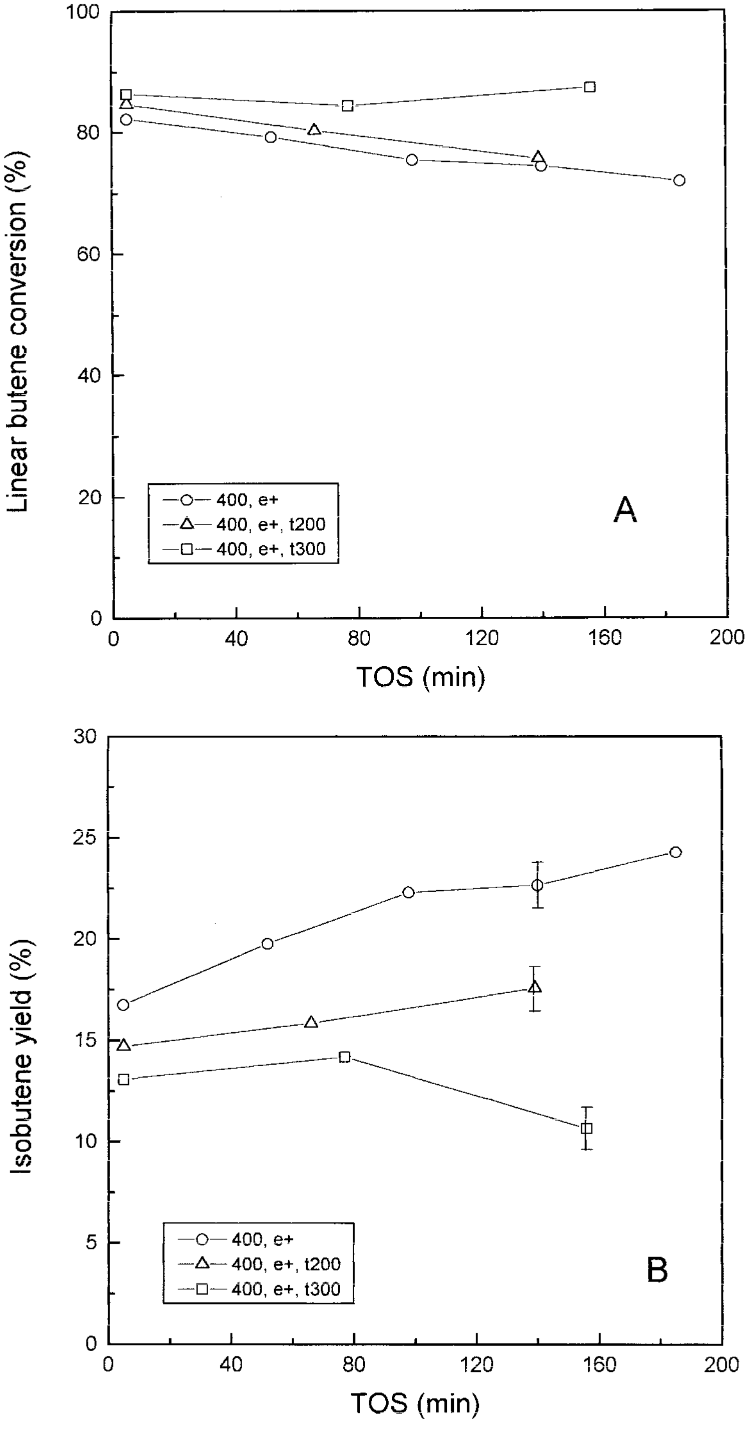

Figure 3. (A) Linear butene conversion and (B) isobutene yield as a function of time-on-stream during the 1-butene skeletal isomerization on ferrierite at 400 °C and feeding the 1-butene stream through a 4 Å molecular sieve bed activated at either 4 h at 200 °C (t200) or 6 h at 300 °C (t300).

improving the isobutene selectivity [11]. By starting feed at 100 °C and then increasing up to 300 °C, a similar catalytic behavior is obtained for both butene streams containing either ethene or propene. Comparing by-product distribution at 5 min with the one obtained when feeding directly over the bed at 300 °C, propene increases and the C_5^+ fraction decreases for the ethene-containing feed. The propene-containing feed shows the C_5^+ fraction practically constant and the propene increment takes place at the expense of propane. At longer times, the C_3 fraction slightly decreases, increasing the C_5^+ one, independent of the feed. Oxidation profiles are similar, showing two well-defined combustion peaks (figure 4). By starting feed at 200 °C and then increasing up to 400 °C, the oxidation profile displays only the high-temperature combustion peak (figure 5).

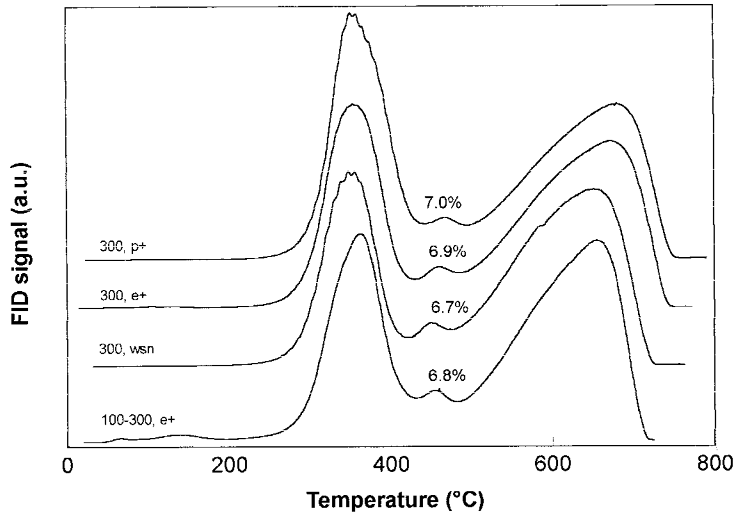

Figure 4. Temperature-programmed oxidation profiles of ferrierite samples coked at atmospheric pressure, 0.15 atm 1-butene partial pressure, and reaction at 300 °C or starting the feed at 100 °C and then increasing it up to 300 °C (100–300). Samples identified according to figure 1. The corresponding carbon contents (%) are also included.

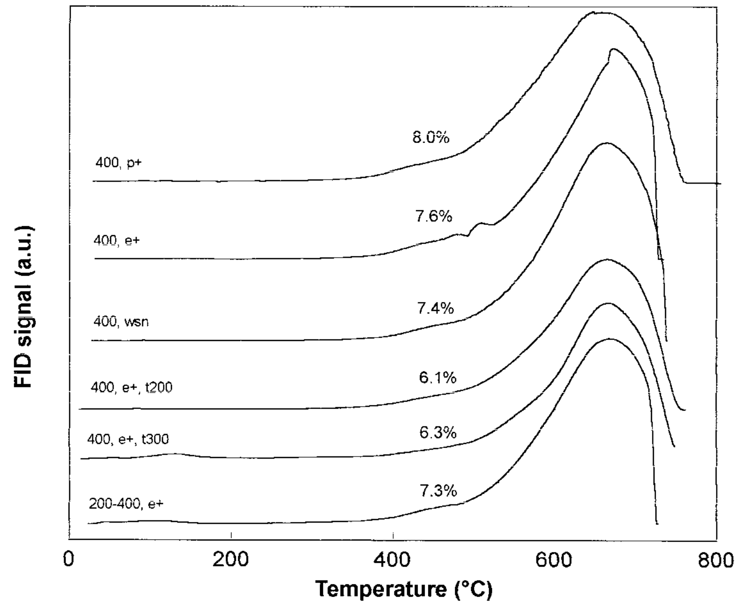

Figure 5. Temperature-programmed oxidation profiles of ferrierite samples coked at atmospheric pressure, 0.15 atm 1-butene partial pressure, and reaction at 400 °C or starting the feed at 200 °C and then increasing it up to 400 °C (200–400). Samples identified according to figures 1 and 3. The corresponding carbon contents (%) are also included.

4. Discussion

Isomerization, disproportionation, coking and hydrogen transfer reactions take place when feeding 1-butene over fresh ferrierite [12]. This fresh material has been considered non-selective, a bimolecular mechanism taking place [13]. The acid strength distribution of H-ferrierite shows two types of acid sites with medium and strong strength, respectively [3,7,14]. The high activity at short time-on-stream has been related to the strongest acid sites [14]. During the first minutes on stream and considering the fresh material, catalytic behavior does not modify significantly when reaction takes place at 300 or 400 °C. This allows us to consider that the strongest acid sites present on the surface govern the catalytic activity at the reaction start.

As a function of time-on-stream, the higher the reaction temperature, the larger the linear butene conversion with a lower isobutene selectivity. An inverse relation between conversion and isobutene selectivity has been previously reported [15]. Nevertheless, the isobutene yield does not significantly change. According to by-product distribution, C_3 (propane plus propene) and C_5^+ fractions are the main ones at 400 °C, while at

300 °C the larger proportion corresponds to the C_5^+ fraction. These results can be understood considering that isomerization and oligomerization-cracking processes occur following different mechanisms as has been previously proposed, the oligomerization-cracking one being favored at higher temperature [16,17]. It can also be considered that the desorption of by-products from oligomeric species present on the surface is favored at high temperature while some species remain adsorbed at lower temperature. A quick deactivation is produced by the formation of carbonaceous deposit, which limits oligomerization and cracking side-reactions and improves the isobutene selectivity [7]. This behavior has been explained considering that the aged material is non-selective, governing a monomolecular mechanism [13]. The largest proportion of carbonaceous deposit is formed during the first 30 min on stream [18]. Carbon content after reaction at 300 and 400 °C varies between 6.7% and 8.0%, only differing 10–15%. This agrees with previous results reporting coke levels between 7% and 9% [6,7,19]. Nevertheless, the light brown color after reaction at 300 °C and the two well-defined combustion peaks in the corresponding oxidation profiles are marked differences with respect to the black color after reaction at 400 °C and the only high-temperature combustion peak. This last peak has been related to a more polymerized and less hydrogenated coke [20]. Preliminary IR results show that the carbonaceous deposit formed after reaction at 400 °C presents a band centered at about $1590\,\text{cm}^{-1}$, commonly ascribed to the carbon–carbon stretching vibration in aromatic rings [21]. This band does not appear in the spectra corresponding to samples after reaction at 300 °C. Consequently, our results allow us to consider that reaction temperature has a strong influence over both conversion level and isobutene selectivity at long times and over the carbonaceous deposit nature, while isobutene yield and coke amount are not significantly modified.

The presence of lower olefins, such as ethene and propene, in the 1-butene feed generates slight differences over the catalytic behavior at 300 °C. The main effect is observed in by-product distribution. Neither methane nor ethane are produced under different conditions. At 400 °C and short time-on-stream, the propene-containing feed produces a C_5^+ fraction practically two times the C_3 one while both fractions are similar when the butene feed contains ethene. This allows us to consider that the 1-butene reaction by-products are formed from oligomers. de Jong *et al.* [22], studying the 1-butene reaction on ferrierite, proposed that initially oligomerization and cracking reactions are favored and the carbonaceous deposit formed has an oligomeric nature, its slow aromatization then occurring. At 300 °C, the C_5^+ fraction is the main one, diminishing the light by-products. This agrees with the retention of species on the surface at low temperature as proposed above. The irreversible adsorption of butenes at 350 °C has been reported [22].

Decreasing ethene concentration in the 1-butene stream by feeding it through the molecular sieve bed, conversion increases while isobutene yield decreases. At short time-on-stream, propene diminishes and the C_5^+ fraction increases; by-product distribution changes at long times, the C_5^+ fraction reaching about 87%. The oxidation profile displays only the high-temperature combustion peak, characteristic after reaction at 400 °C, but the amount of carbonaceous deposit is smaller. These results can be explained considering that by decreasing ethene concentration in the stream fed, a larger amount of acid sites are accessible to butene molecules. A high acid-site concentration favors oligomerization and side reactions [9]. Considering the lower reactivity of ethene with respect to butene [23], the presence of ethene favors coking while formation and desorption of by-products improve by decreasing ethene concentration.

The presence of water by saturating the nitrogen stream improves activity but isobutene yield decreases. By-product distribution modifies only slightly at 400 °C and short times, the propane : propene ratio changes from 1 : 1 to 1 : 3, the total C_3 fraction remaining practically constant. The carbon content slightly decreases. These results can be associated with a change in the environment of acid sites. Preliminary results, adding hydrogen to the nitrogen stream during pretreatment and/or reaction but keeping the 1-butene partial pressure, show that neither catalytic behavior nor product distribution significantly change. For other catalytic systems, the water addition in feed diminishes deactivation and improves isobutene selectivity [24,25]. The presence of water during the ferrierite pretreatment affects the coke nature, probably by modifying the active sites [26]. IR characterization of ferrierite showed the presence of OH assigned to Brönsted acid sites, identifying two types of sites [27,28]. The acid sites located on the external surface of zeolite crystallites are non-selective and responsible for side reactions, while isomerization takes place on the internal acid sites, which are selective [5]. Both catalytic activity and isobutene selectivity have been related to the acid-site density [9] and to the space around these sites [8]. The presence of water previous to reaction and at its beginning could modify the acid-site environment, then affecting the catalytic behavior and the carbonaceous deposit nature at longer times.

5. Conclusions

At short time-on-stream (5 min), the strongest acid sites, independent of the operating conditions in the studied ranges, govern the catalytic behavior of ferrierite during the skeletal isomerization of linear butene. At longer times, temperature mainly defines the conversion level. The higher the temperature, the larger the linear butene conversion. A direct relation between temperature and carbonaceous deposit formed during reaction is also observed, being the main effect over its nature rather than over the amount. At 400 °C, the oxidation profile displays only the high-temperature combustion peak, the deposit showing mainly an aromatic nature. The presence of lower olefins in the fed stream modifies both catalytic activity and by-product distribution. By decreasing ethene concentration in the butene feed, the C_5^+ fraction in the product stream increases, being smaller than the carbonaceous deposit formed during reaction. Using a nitrogen stream saturated with water during both pretreatment and reaction, the catalytic activity increases and the coke amount slightly diminishes, but the isobutene yield is unfavored. This behavior could be related to a change in the acid-site environment.

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