Deactivation of ferrierite during the skeletal isomerization of linear butenes

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Received 26 June 2000; accepted 2 November 2000

Deactivation of ferrierite during the skeletal isomerization of 1-butene at atmospheric pressure and 0.15 atm 1-butene partial pressure was studied. At 300 °C, the carbon content shows a sharp increase during the first 30 min-on-stream, with a slower growth thereafter. Temperature-programmed oxidation profiles corresponding to different times-on-stream are similar, showing two well-defined combustion peaks centered at about 325 and 640 °C, respectively. When starting the 1-butene feed with the catalytic bed at 100 or 200 °C and then increasing the temperature up to 300 °C, no significant difference is observed, neither in carbon content nor in oxidation profiles. Important differences in the profiles are observed by comparing at the same time at each temperature. The lower the temperature, the higher the reactivity toward oxidation at low temperature. The carbonaceous deposit formed at 100 °C shows the main combustion peak at the lowest temperature (135 °C) and a more olefinic character; it could be related to a strong adsorption of reactant molecules. At 200 °C, the proportion of saturated species associated to oligomers increases; while at 300 °C, coke shows both aromatic and olefinic species.

KEY WORDS: skeletal isomerization; isobutene; ferrierite; deactivation; coke characterization

1. Introduction

In the last few years, the skeletal isomerization of linear butenes has achieved an increasing practical interest as an alternative route for the production of isobutene, which is an important material for the production of methyl *tert*-butyl ether used as a booster of the octane number for reformulated gasolines. That isomerization reaction takes place on acid catalysts. The most suitable zeolitic materials are 10-membered ring molecular sieves with pore diameters between 40 and 55 nm [1,2]. For materials with shape selectivity, some authors consider that pore structure plays a more important role than acidity to improve the isobutene selectivity [1,3]. Ferrierite, a zeolite with a bidimensional pore structure of 10-membered rings (42×54 nm) intersected by 8-membered rings (35×48 nm), has been presented as one of the best materials [4]. However, ferrierite shows a high activity with a low selectivity to isobutene at short time-on-stream, improving this selectivity when a carbonaceous deposit has been formed [5,6]. This deposit suppresses undesirable side reactions such as dimerization and cracking, thus increasing isobutene selectivity [7]. Between 6 and 10% [7–9], the carbon content reaches significant levels. Characterization of the carbonaceous deposit showed an aromatic nature in essence, although the presence of olefinic species has also been detected [10].

The high activity reached with ferrierite at a short time can be diminished, improving the isobutene selectivity, by starting the 1-butene feed with the catalytic bed at a low temperature and then increasing it up to the reaction one [11]. The carbonaceous deposit thus formed shows a more olefinic than aromatic nature, while coke is more aromatic when the reactant is directly fed with the bed at the reaction temperature. Catalytic behavior of ferrierite during the 1-butene isomerization at different temperatures and the amount of coke formed [8] as well as the analysis for times between 2 and 18 h [10] and the characterization of adsorbed species at low temperatures [12,13], have been reported. Nevertheless, there are no data available about deactivation and/or characterization of the carbonaceous deposit when reaction starts at different catalytic bed temperatures.

In this paper, ferrierite behavior during the 1-butene isomerization at atmospheric pressure and 0.15 atm 1-butene partial pressure is systematically studied, the alkene feed starting at different bed temperatures. Characterization of the carbonaceous deposit by temperature-programmed oxidation and Fourier transform infrared spectroscopy (FTIR) allows us to analyze the effect of feeding the reactant at different bed temperatures.

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 with diffraction spectrum range $0^\circ < 2\theta < 60^\circ$.

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

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Table 1
Operating conditions during the 1-butene isomerization on ferrierite at atmospheric pressure and 0.15 atm 1-butene partial pressure.

	Experiment							
	1	2	3	4	5	6	7	8
Temperature (°C)	300	300	300	300	100	100	200	200
Time-on-stream (min)	10	30	60	120	10	30	10	30

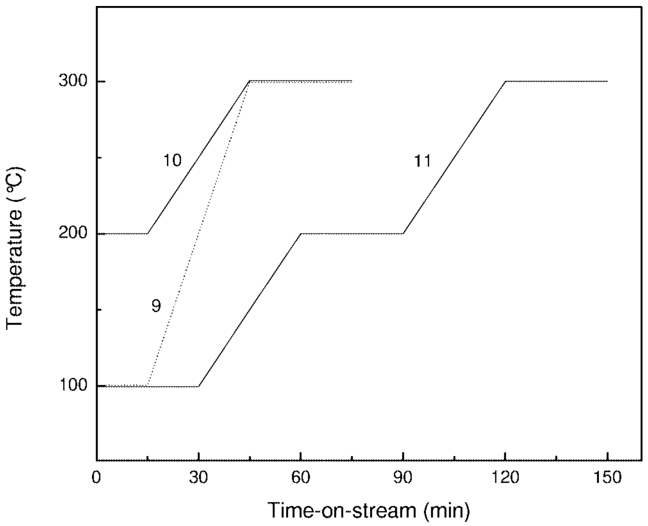


Figure 1. Operating conditions during the 1-butene isomerization on ferrierite at atmospheric pressure and 0.15 atm 1-butene partial pressure. Experiments starting the reactant feed at a low bed temperature and then increasing it.

nitrogen stream at 17.3 °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. Table 1 shows experiments carried out at different temperatures and times, while figure 1 displays other ones starting the reactant feed at a low bed temperature (100 or 200 °C), then increasing it. 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, selectivity to isobutene, and isobutene yield were calculated on a carbon basis. The catalytic activity is expressed as *n*-butenes conversion, grouping together the three linear butene isomers. It is based on the fact that, under operating conditions, isomerization of 1-butene to 2-butenes reaches quickly the equilibrium via double-bond migration.

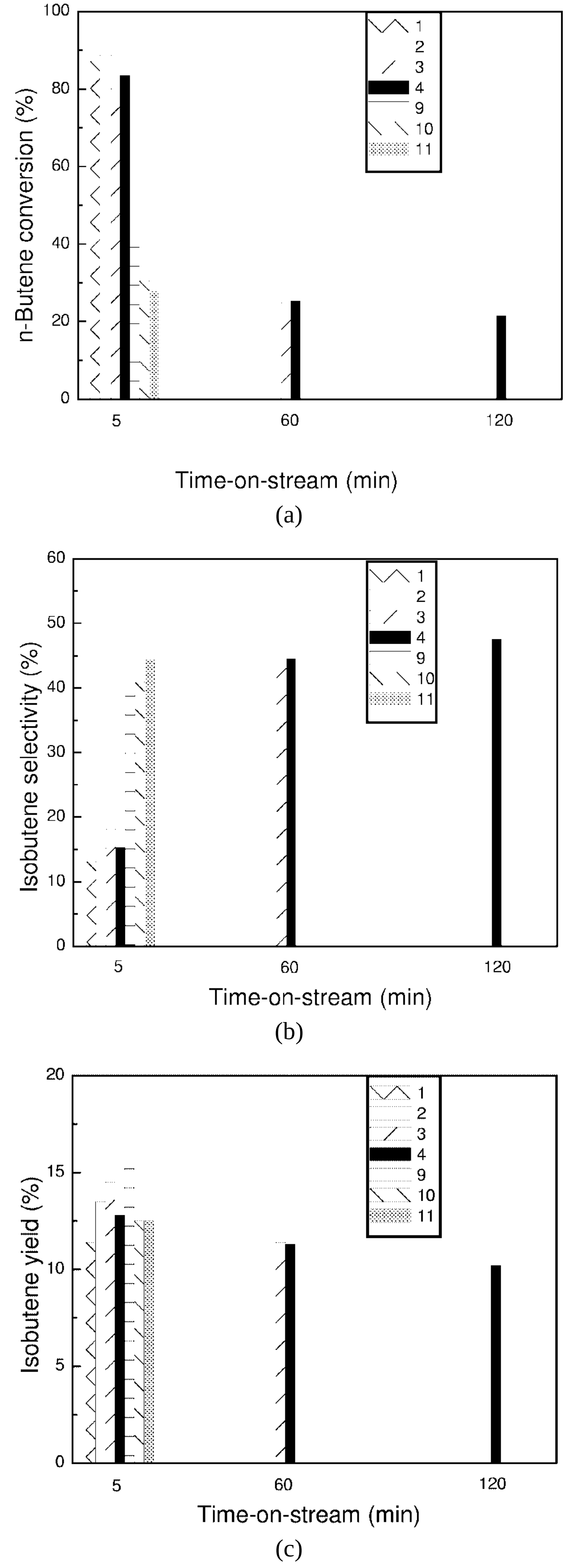
The carbonaceous deposit formed was characterized by temperature-programmed oxidation in an apparatus specially designed to improve sensitivity and resolution [14]. Combustion products were completely converted to methane on a nickel catalyst, methane being continuously analyzed by a flame ionization 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 total conversion of carbon monoxide and carbon dioxide into methane.

In order to obtain additional characterization of the carbonaceous deposit on catalysts, FTIR measurements were carried out at room temperature in a Shimadzu FTIR 8101 M single beam spectrometer. Coked samples were powdered and diluted to 5% in potassium bromide; then, a thin disk (about 15 mg cm^{-2}) was placed in an infrared cell provided with calcium fluoride windows. Infrared spectra were recorded in the 4000–1200 cm^{-1} range with a 4 cm^{-1} instrument resolution.

3. Results and discussion

Figure 2 shows linear butenes conversion (a), selectivity to isobutene (b), and isobutene yield (c) under different operating conditions. Feeding 1-butene with the catalyst bed at 300 °C (experiments 1–4), conversion of about 85%, 15% isobutene selectivity, and 13% isobutene yield are reached for the first analysis (5 min). Differences at this time could be related to the large conversion and also to the time considered as the start of the reaction. By increasing time-on-stream (experiments 3–4), conversion decreases below 30% with an increase in the isobutene selectivity. It is the characteristic behavior of ferrierite previously reported [5,7]. When feeding reactant with the bed at 100 or 200 °C (experiments 5–6 and 7–8, respectively), isobutene does not appear in the product stream, the double-bond isomerization products (2-butenes) being the only ones detected. Starting feed at a low bed temperature and then increasing it up to 300 °C (experiments 9–11), a lower conversion and a better selectivity with similar isobutene yield compared to experiments directly feeding at 300 °C are reached for the first analysis. The activity decrease at a short time could be due to an irreversible adsorption of reactant molecules on the strong acid sites [12] and/or to the oligomerization of adsorbed species [15]. For all the experiments, the *cis*-2-butene/*trans*-2-butene ratio remained practically constant (0.63). This might suggest that the skeletal isomerization of butenes takes place through a monomolecular mechanism, as it has been considered when that ratio is lower than 1 [16].

Carbon content as a function of time-on-stream under different conditions is shown in figure 3. There is a sharp increase for time below 30 min, then, reaching levels between 6 and 7%, independent of the operating conditions. According to these results, the largest proportion of the carbonaceous deposit is formed during the first minutes, with a slower growth at a longer time. Coke between 6 and 10% for times longer than 6 h has been previously reported [7,9]. A slow growth with time-on-stream has also been mentioned but comparing deposits formed at a long time [9,10]. The only reference of coke build-up on ferrierite as a function of time corresponds to kinetic experiments carried out under



(a)

(b)

(c)

Figure 2. (a) Linear butenes conversion, (b) selectivity to isobutene and (c) isobutene yield during the 1-butene skeletal isomerization on ferrierite at several times-on-stream at 300 °C. Operating conditions shown in table 1 and in figure 1.

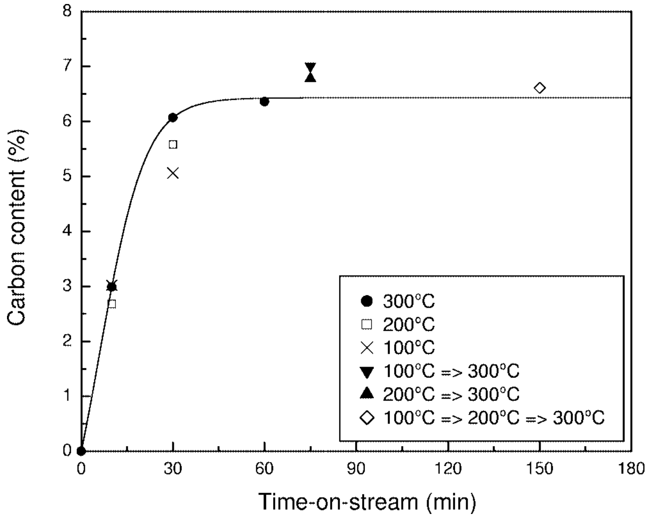


Figure 3. Carbon content as a function of time-on-stream. Operating conditions shown in table 1 and in figure 1.

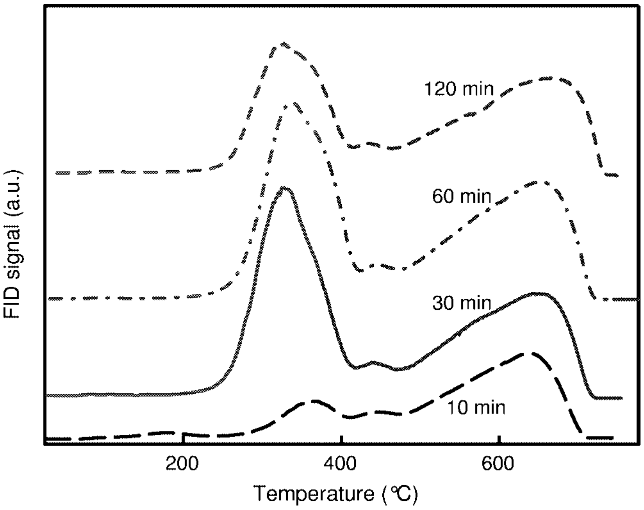


Figure 4. Temperature-programmed oxidation profiles of ferrierite samples coked at atmospheric pressure, 0.15 atm 1-butene partial pressure and 300 °C during different times-on-stream.

static conditions [10]. According to these authors, it could be different from flow conditions. Our results under flow condition completely agree with the latter. Considering at 30 min-on-stream, the higher the temperature, the larger the carbon content. However, it does not verify for 10 min, levels being similar for the different temperatures.

Figures 4–7 display temperature-programmed oxidation profiles under different operating conditions. Profiles corresponding to 300 °C at different times-on-stream (figure 4) and to 30 min at 300 °C after starting reactant feed at different bed temperatures (figure 5), are qualitatively similar. Two well-defined combustion peaks (their maxima centered at about 315–335 and 630–650 °C, respectively) and a smooth one between them, are observed. The profile corresponding to 10 min at 300 °C is the only one that shows a difference, its low-temperature combustion peak is significantly lower than that for the other profiles; this is not hap-

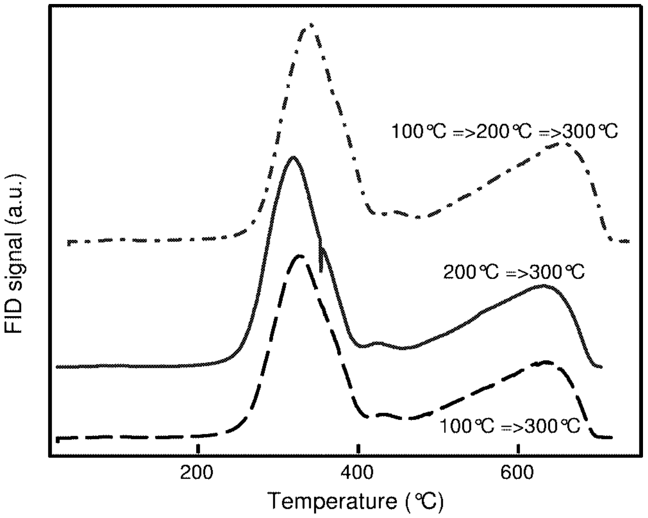


Figure 5. Temperature-programmed oxidation profiles of ferrierite samples coked at atmospheric pressure, 0.15 atm 1-butene partial pressure and 30 min at 300 °C after starting the reactant feed at different bed temperatures.

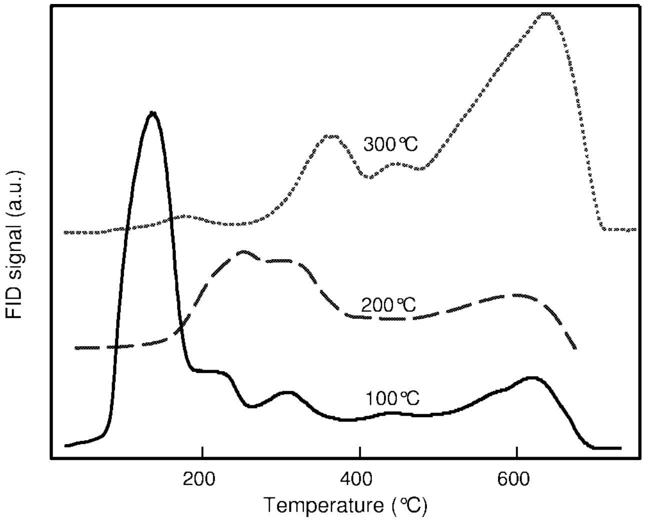


Figure 6. Temperature-programmed oxidation profiles of ferrierite samples coked at atmospheric pressure, 0.15 atm 1-butene partial pressure and 10 min at different temperatures.

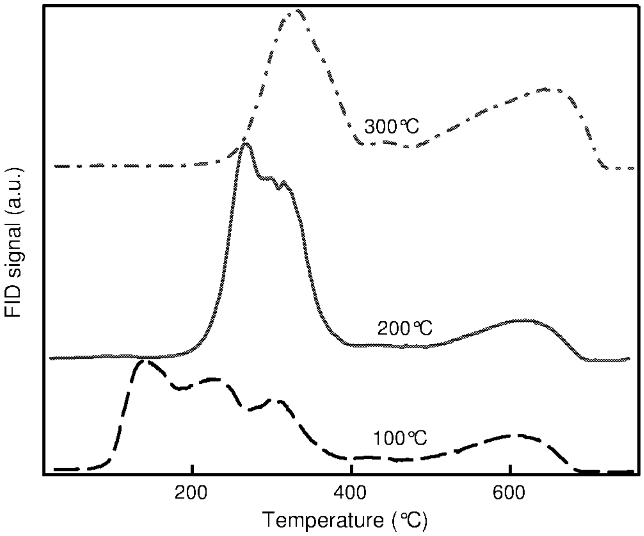


Figure 7. Temperature-programmed oxidation profiles of ferrierite samples coked at atmospheric pressure, 0.15 atm 1-butene partial pressure and 30 min at different temperatures.

pening with the peak centered at high temperatures. It makes interesting to analyze the behavior at a short time-on-stream feeding reactant at different bed temperatures.

Figure 6 shows the profiles corresponding to 10 min, allowing the comparison with the behavior at 300 °C previously described. After 10 min at 200 °C, the high-temperature combustion peak is significantly lower and slightly shifted to a lower temperature. The largest proportion of the carbonaceous deposit corresponds to a broad peak or two overlapped peaks centered between 250 and 305 °C. This behavior is even more evident for the 100 °C corresponding profile. The largest proportion of the carbonaceous deposit corresponds to the lowest-temperature combustion peak with a maximum at 135 °C, while peaks centered at about 220 and 305 °C as well as the high-temperature one also appear. Figure 7 allows the analysis for 30 min-on-stream at different temperatures. Remarkable differences still remain between profiles, mainly at combustion temperatures below 400 °C. The profile corresponding to 100 °C shows the three peaks centered at 135, 220 and 305 °C, respectively, with slightly decreasing proportions. At 200 °C, a broad peak or overlapped ones are observed with the main maximum at 265 °C and shoulders at higher temperatures. Finally, a large combustion peak centered at 325 °C is observed for 300 °C. The high-temperature combustion peak mainly changes its proportion, showing a slight shift towards a higher temperature for 300 °C. Results corresponding to 10 and 30 min indicate a change in the nature of carbonaceous deposit. The lower the temperature, the lower the combustion temperature of the largest proportion of the deposit formed. It could be associated to the presence of more hydrogenated species. Irreversible adsorption of reactant molecules at temperature below 350 °C [12] as well as the strong adsorption of such species or the slow isobutene desorption favoring oligomerization reactions [15], have been reported. These considerations may explain our results.

Temperature-programmed oxidation profiles (figure 4) correspond to the sharp increment of the carbonaceous deposit at times below 30 min and the slower growth thereafter (figure 3). In this slight-increase zone, carbon contents corresponding to long times under different conditions (figure 5) are found. Similar carbon contents are reached after 10 and 30 min independently of the temperature, but oxidation profiles present remarkable differences (figures 6 and 7). These results show the strong influence of temperature on the nature of the carbonaceous deposit.

The nature of the deposit formed during linear butene isomerization on ferrierite at temperatures between 350 and 420 °C deserves a special analysis. Xu et al. [10] reported an aromatic character, although in the infrared characterization they also found bands assigned to olefinic species. An initial paraffinic character of the deposit and then its slow aromatization were reported by de Jong et al. [12]. Finally, Andy et al. [17] proposed a pseudo-monomolecular reaction mechanism involving benzylic carbocations and considered that the carbonaceous deposit corresponds mainly to methylaromatics. Previous results, including characterization of the carbonaceous deposit by temperature-programmed oxidation and diffuse-reflectance infrared spectroscopy, showed the presence of both aromatic and olefinic species, its proportion depending on operating conditions [18]. Preliminary FTIR analysis over the samples feeding at different bed temperatures agree with the temperature-programmed oxidation results. At 300 °C, bands at 1515 and 1630 cm^{-1} assigned to aromatic and olefinic groups, respectively [17,19], indicate the presence of both species in the deposit. At 200 °C, the 1515 cm^{-1} band decreases, the 1630 cm^{-1} one remains, and other well-defined bands appear at 2960 and 2868 cm^{-1}, associated to stretching vibrations of CH in saturated species [19]. Aliphatic coke character has been previously related to butene oligomers [12]. Finally, at 100 °C, the 1515 cm^{-1} band is even weaker, the strongest band appearing at 1625 cm^{-1} and another one at 1399 cm^{-1}, assigned to linear butenes and/or olefinic species [20,21]. The 2960 and 2868 cm^{-1} bands only appear at 30 min. Along with this characterization, it can be considered that at 100 °C and a short time adsorbed species would be mainly associated to reactant molecules and/or oligomers, the olefinic character of the carbonaceous deposit prevailing. At longer times or feeding at 200 °C, a stronger influence of saturated species probably related to butene oligomers is observed. Finally, at 300 °C, the deposit presents both aromatic and olefinic species.

4. Conclusions

By studying the deactivation processes of ferrierite during the skeletal isomerization of linear butenes, the largest proportion of the carbonaceous deposit is formed during the first minutes of operation (up to 30 min). Moreover, its nature is strongly influenced by the temperature of the catalytic bed when starting butene feed. The lower the temperature, the higher the reactivity toward oxidation at low temperatures. At 100 °C, the carbonaceous deposit shows a more olefinic character; at 200 °C, the proportion of saturated species associated to oligomers increases, and finally both aromatic and olefinic species are present at 300 °C.

Acknowledgement

The authors are indebted to JICA (Japan International Cooperation Agency) for the donation of the FTIR equipment to CENACA (National Catalysis Center) and to TOSOH for the provision of the ferrierite sample. The authors thank Dr. C. Querini and Mr. A. Díaz for their help in doing TPO and FTIR analysis, respectively. The financial assistance of CAI+D (UNL) and CONICET is also acknowledged.

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