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Tungsten-ferrierite catalysts prepared by impregnation and ion-exchange: Characterization and activity during the skeletal isomerization of linear butenes

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Tungsten-ferrierite catalysts were prepared by impregnation and ion-exchange. Potassium (KF), ammonium (AF), and protonic (HF) ferrierites were used as starting materials. Characterization of impregnated catalysts shows reduction peaks characteristic of tungsten species, whereas the absence of a peak in the corresponding profiles of the exchanged material indicates such species were incorporated into the framework. For impregnated materials, the tungsten species-surface interaction is not strong. Catalytic performance during the linear butene skeletal isomerization at 300 °C and at atmospheric pressure was measured. Exchanged materials reach both conversion and isobutene yield larger than the impregnated ones. Samples prepared from AF and HF practically display the same catalytic behavior at 5 min, being associated with the presence of strong acid sites. Tungsten-impregnated KF does not reach a high activity at a short time-on-stream (TOS), showing a particular by-product distribution related to the absence of strong acid sites. Even though exchanged samples starting from KF show the HF characteristic behavior, differences at 5 min appear. By-product distributions allow us to consider their formation from dimers and/or oligomers. At 5 min, the C_5^+ fraction is the main one, following propene, propane, and butane in similar proportions. Over the "clean" surface, propene could be involved in other reactions considering its high reactivity. At a long TOS, both the C_5^+ fraction and propane decrease, whereas propene increases, verifying the bimolecular mechanism.

KEY WORDS: tungsten-ferrierite; impregnation; ion-exchange; skeletal isomerization; isobutene.

1. Introduction

Ferrierite shows one of the best catalytic performances during the skeletal isomerization of linear butenes [1]. The characteristic behavior of this zeolite shows a high activity with low isobutene selectivity at a short TOS; then, conversion decreases and selectivity increases with TOS. This behavior has been related to the carbonaceous deposit formation [2,3], the type of acid sites [4], the space around the acid site [5], and the acid-site density [6]. The reaction mechanism of linear butene skeletal isomerization on ferrierite remains under discussion. Nevertheless, the fresh material is accepted as non-selective, whereas the aged one is considered selective. Topics related to ferrierite deactivation have constituted the main interest, especially in order to understand the isobutene selectivity improvement with TOS. An exhaustive analysis of deactivation of solid acid catalysts, including ferrierite, during the linear butene skeletal isomerization has recently been published [7].

Catalytic improvement of KF and AF by tungsten-species impregnation, following the incipient-wetness technique and using both tungstic acid and ammonium metatungstate as tungsten precursors, was previously reported [8]. The presence of tungsten species on ferrierite improves the catalytic behavior without modifying acidity profiles corresponding to the unpromoted materials [9]. Tungsten species impregnated on KF promotes catalytic activity, but without reaching a high conversion at a short TOS. Then the zeolite form used as starting material in catalyst preparation could be an important parameter. In order to characterize exchange sites in the ferrierite framework, the location of Cu cations in the dehydrated copper ion-exchanged ferrierite [10] and Ni ion sites in hydrated and dehydrated forms of nickel-exchanged ferrierite [11] were analyzed. 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 [5]. More recently, the catalytic properties of ferrierite exchanged with alkaline earth metals in the *n*-butene skeletal isomerization [12] and the selective formation of alkenes through the *n*-heptane cracking on Ca-exchanged ferrierite [13] were reported. Nevertheless, there are no available data on the influence of the catalyst preparation technique on its catalytic performance.

The effect of the preparation technique of tungsten-ferrierite catalysts on their behavior during the linear butene skeletal isomerization is studied in this paper.

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Impregnation following the incipient-wetness technique and ion-exchange are compared. KF, AF and HF are used as starting materials. Characterization by temperature-programmed reduction (TPR) and the catalytic test of 1-butene reaction at 300 °C and at atmospheric pressure are done in order to explain material behavior.

2. Experimental

KF and AF samples were provided by TOSOH, Japan (samples HSZ-720KOA and HSZ-720NHA, respectively). The SiO_2/Al_2O_3 molar ratio was 17.8; AF has Na_2O and K_2O concentrations 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 $0 < 2\theta < 60°$ [8].

Tungsten-ferrierite samples were prepared by two techniques: incipient-wetness impregnation and ion-exchange. Tungsten (VI) dichloride-dioxide (Aldrich) was used as a tungsten precursor, selected mainly for ion-exchange. Solutions with the desirable tungsten concentration were prepared. KF, AF and HF (ferrierite in the protonic form obtained by calcining AF at 550 °C) were impregnated and maintained for 4 h at room temperature and then dried overnight in an oven at 110 °C. Tungsten loadings were 2.4 wt% on KF and 0.8 wt% on both AF and HF. These samples were identified as W/KF, W/AF and W/HF, respectively. KF and AF were used as starting materials for ion-exchange. Typical exchange conditions were: 1 g : 11 ml solid–liquid ratio, 60 °C, pH between 4 and 5, and continuous stirring for 6 h. Then the exchanged material was filtered, washed with deionized water until free of chloride ions, and dried overnight in an oven at 110 °C. One or two exchanges were made, and two different concentrations were used. Table 1 shows exchange parameters and the sample identification.

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 ($60\,ml\,min^{-1}$) plus air ($50\,ml\,min^{-1}$) stream, heating at $9.6\,°C\,min^{-1}$ and holding for 60 min at 600 °C. Then samples were cooled to room temperature in an argon stream and finally heated at $10\,°C\,min^{-1}$ up to 950 °C in a 1.8% hydrogen in argon stream.

Table 1
Tungsten concentration in the exchange solution, exchange steps, tungsten loading on solids, and sample identification.

Starting material	W in the exchange solution (M)	Exchange steps	W loading (wt%)	Sample identification[a]
KF	0.042	1	4.8	$W_{L1}KF$
KF	0.042	2	6.9	$W_{L2}KF$
KF	0.101	1	7.7	$W_{H1}KF$
AF	0.042	2	n.d.	$W_{L2}AF$

[a] The first subindex is referred to the exchange solution concentration (L: low, H: high), and the second one to the exchange number (1 or 2).

The catalytic behavior during the 1-butene skeletal isomerization 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. Samples were pretreated *in situ* under the same previous conditions. After heating, samples were cooled to 300 °C in a nitrogen stream. For reaction, a pure 1-butene stream was co-fed with nitrogen at 0.15 atm 1-butene partial pressure. 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 30 min. From these data, catalytic activity, selectivity to isobutene, 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-butene to 2-butene isomerization quickly reaches the equilibrium *via* double-bond migration.

3. Results and discussion

Previous TPR characterization of AF and KF does not show a reduction peak [9]. Figure 1 displays TPR profiles corresponding to impregnated and exchanged materials. Impregnated samples present reduction peaks associated with tungsten species; differences appear according to the impregnated ferrierite form and the tungsten loading. The W/AF corresponding profile displays two overlapped peaks with maxima centered at about 620 and 740 °C, respectively. W/HF, with the same tungsten loading, presents a broad reduction peak beginning at 650 °C, which could be considered as the latter of two overlapped peaks, decreasing the first one and shifting both maxima to higher temperatures, 690 and 780 °C, respectively. The largest tungsten loading on KF produces higher peaks but are centered at the same previous temperatures; the largest peak is the one with a maximum of 690 °C, and a slight shoulder appears at about 510 °C when starting the reduction. This profile is similar to the one corresponding to WO_3 reduction, which starts below 500 °C and shows peaks with maxima at 656 and 763 °C, both shifting to higher temperatures by increasing the sample size [14]. The presence of more than one peak would indicate that reduction can take place in steps, even though the relationship between areas under reduction peaks does not allow one to consider the $W^{6+} \Rightarrow W^{4+} \Rightarrow W^0$ sequence. A tungsten species–surface interaction can

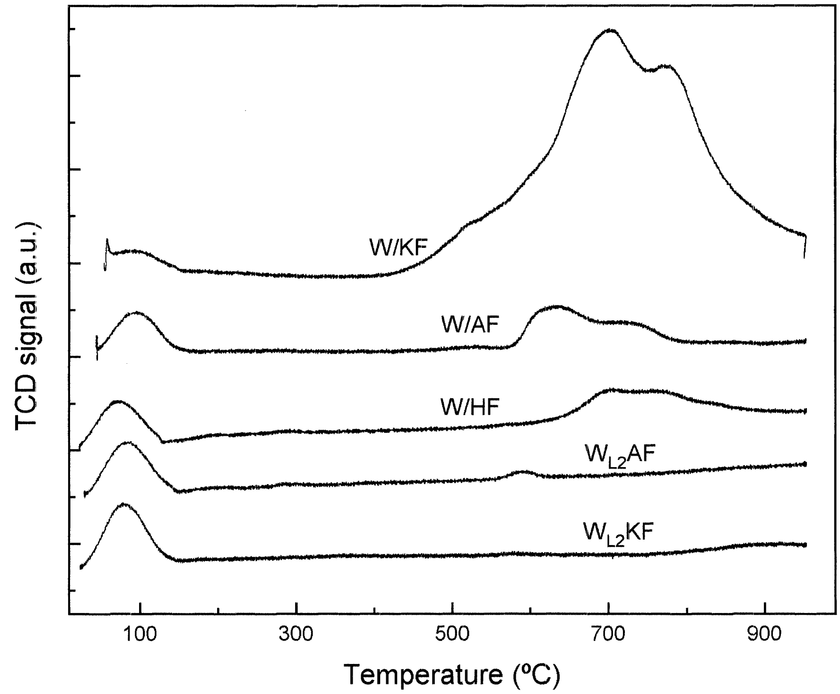

Figure 1. TPR profiles of impregnated and exchanged samples.

occur but it does not seem strong, as reported for the W/alumina system in which tungsten-species reduction shifts to higher temperatures because of a strong interaction [15,16]. Tungsten-species reduction on AF and HF starts at a higher temperature; it can be associated with the presence of disperse monomeric species, which can be present according to the tungsten precursor used and the low tungsten loading obtained. Reduction of highly dispersed tungsten monomeric species on support as alumina is difficult [15]. HF is the ferrierite form that stabilizes the W^{6+} state in a higher degree, practically allowing the reduction only in one step, as supposed when observing the broad peak. For the W/alumina system, the interaction between tungsten oxide and alumina prevents the WO_3 crystallite formation necessary to stabilize lower oxidation states [16]. Exchanged samples practically do not show any reduction peak, only a slight shoulder at about 590 °C for $W_{L2}AF$ allowing one to consider if tungsten has been incorporated into the zeolite framework.

Figure 2 presents the catalytic behavior of samples prepared from AF and HF. The performance of HF without tungsten is taken as a reference, being the characteristic behavior of ferrierite: a high conversion with a low isobutene selectivity at a short TOS, decreasing activity quickly and improving selectivity as a function of TOS [2]. At 5 min, the behavior of different samples does not change significantly. Previous results related it to strong acid sites present on the surface, which would govern the reaction [17]. At a long TOS, differences appear. W/AF slightly promotes both activity and isobutene yield compared to the unpromoted material, agreeing with previous results using tungstic acid as a precursor [8]. W/HF produces a lower conversion above 60 min and the lowest isobutene yield, which decreases as a function of TOS. $W_{L2}AF$ reaches the largest values of both conversion and isobutene yield. The largest amount of carbonaceous deposit is formed during the first 30 min of reaction [18]. It was reported that the catalytic performance of materials can be influenced by the increased spatial constraints inside the pores produced by coke deposition [2,6], as well as by the space around the active acid sites and its density [5,6]. Consequently, an effect of the carbonaceous deposit over the catalytic behavior at a long TOS could be initially considered.

Figure 3 shows the catalytic behavior of samples prepared from the potassium ferrierite form. KF is inactive in the linear butene skeletal isomerization, whereas the tungsten-species impregnation promotes both activity and isobutene yield. This qualitatively agrees with previous results obtained by impregnating KF with other tungsten precursors [8]. Working with Mo, W and Cr cations supported on silica, it was stated that acidity and cation reducibility determine activity and selectivity during the butene skeletal isomerization reaction [19]. The presence of tungsten species on AF and KF, using tungstic acid and ammonium metatungstate as precursors, does not significantly modify the acid-strength distribution of the corresponding material without tungsten, keeping the total acidity practically constant [9]. Nevertheless, the catalytic performance can be influenced not only by acidity and acid-strength distribution, but also by the type of acid sites [4]. Tungsten impregnation on alumina promotes the butene skeletal isomerization without modifying the acidity profile of

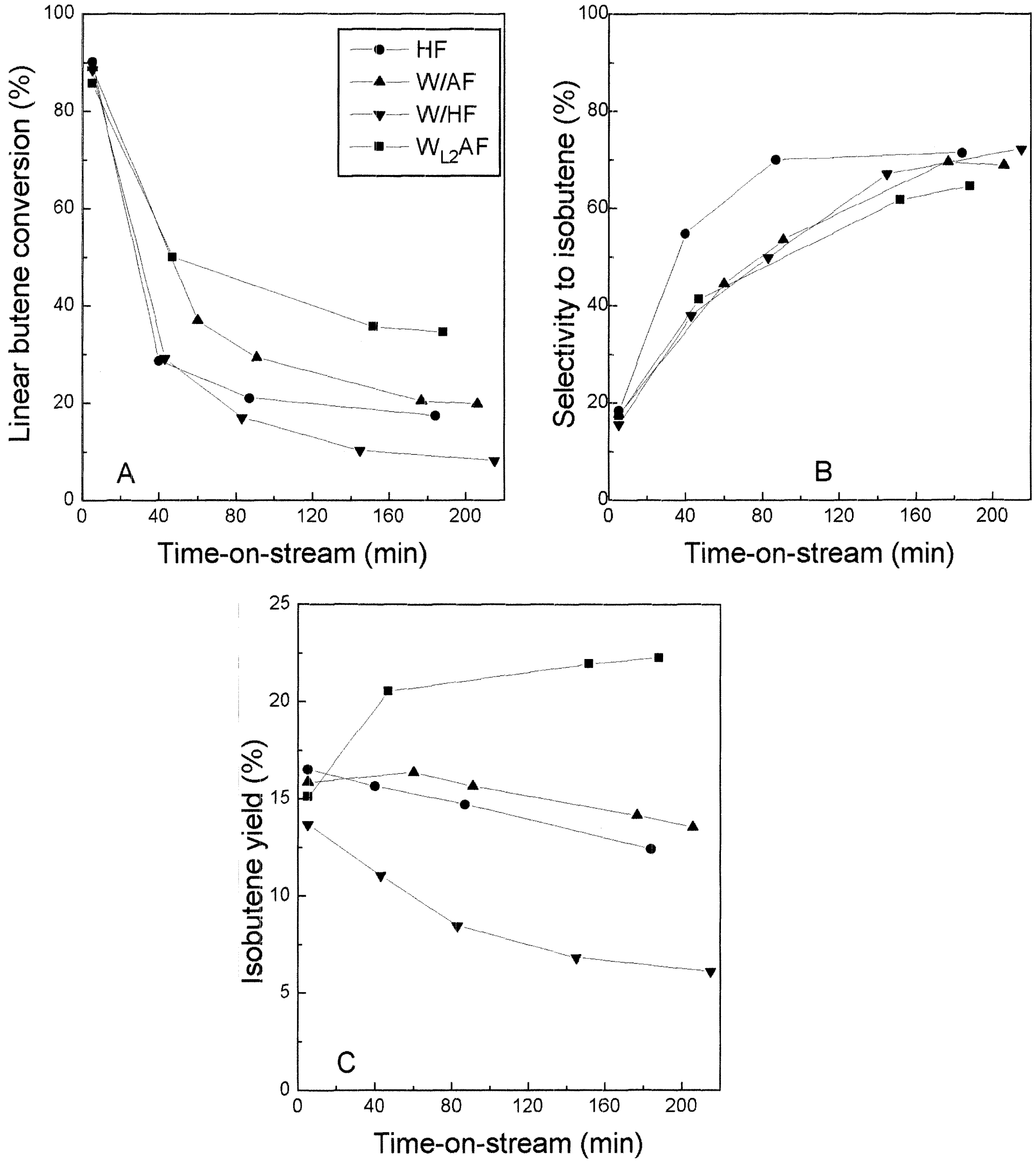

Figure 2. (A) Linear butene conversion; (B) selectivity to isobutene; and (C) isobutene yield as a function of TOS during the 1-butene skeletal isomerization on samples prepared from AF and HF. Activity test at 300 °C, 1 atm, and 0.15 atm 1-butene partial pressure.

alumina; this behavior is explained when considering Lewis acid sites transformed into Brønsted acid sites [20]. Brønsted acidity was associated with WO_3 species or well-dispersed cations and considered essential when the butene skeletal isomerization takes place through an alkoxide intermediate [19]. On ferrierite, the isobutene formation was related to the concentration of Brønsted acid sites, whereas Lewis acid sites favor butene dimerization and oligomerization [21]. W/KF does not reach a high activity at 5 min, showing a good stability. This behavior was explained by considering the absence of strong acid sites [9]. These acid sites were related to the high activity at a short TOS, favoring side-reactions such as oligomerization and cracking, which are responsible for diminishing the isobutene selectivity [2]. Exchanged samples improve both activity and isobutene yield more than the impregnated one, as shown in figure 3. This agrees with results reported by studying the butene isomerization on Cr-promoted SAPO catalysts, giving the exchanged material a better catalytic performance than the impregnated one [22]. The largest difference for W/KF samples is the catalytic behavior similar to the HF corresponding one, with a high activity at a short TOS and then diminishing. Nevertheless, these samples show differences in activity and isobutene yield at 5 min. Successive exchanges do not favor the catalytic performance. The higher the concentration of exchange solution, the larger both the activity and isobutene yield. Considering that TPR profiles corresponding to exchanged samples do not show a reduction peak, the catalytic behavior cannot be associated with the tungsten-species reducibility. Therefore, the effect of the presence of tungsten species on acidity has to be considered. Metal cations, such as Co, Mn and Zn,

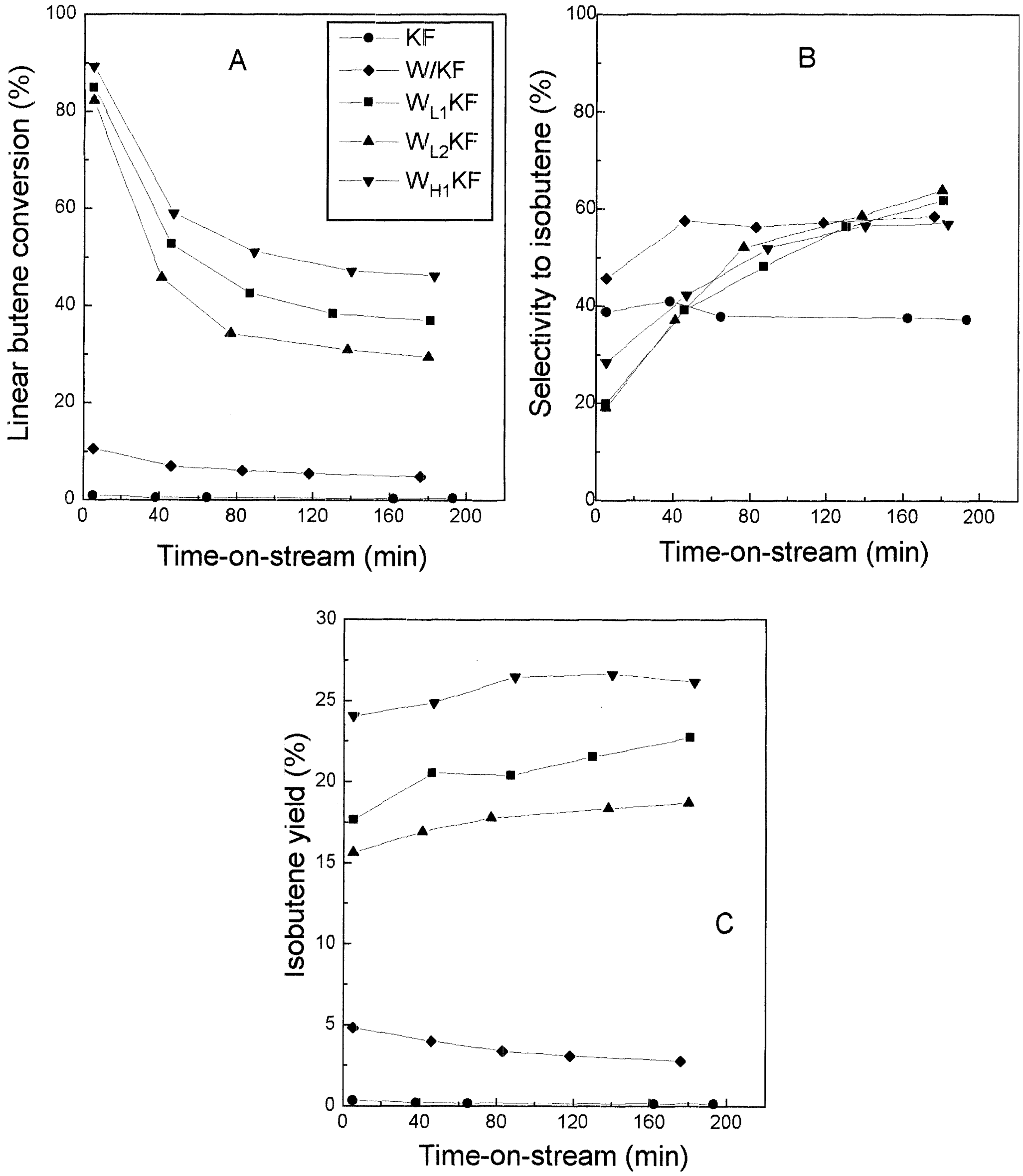

Figure 3. (A) Linear butene conversion; (B) selectivity to isobutene; and (C) isobutene yield as a function of TOS during the 1-butene skeletal isomerization on samples prepared from KF. Activity test at 300 °C, 1 atm, and 0.15 atm 1-butene partial pressure.

incorporated by ion-exchange into the aluminophosphate framework structure, create acidic sites [23]. By studying catalytic properties of ferrierite exchanged with alkaline earth metals during the linear butene skeletal isomerization, an adequate balance between Brønsted and Lewis acid sites is necessary in order to enhance the isobutene yield [12]. Preliminary results of ammonia temperature-programmed desorption would indicate the presence of strong acid sites on W/KF samples explaining their behavior. Differences at 5 min suggest tungsten present in the framework could also modify the environment of active sites and/or its density, thus influencing the catalytic performance as mentioned above.

Isobutene selectivity remains practically constant with TOS for W/KF, as does its activity, associated with acid sites present on this sample. Isobutene selectivity shows no change with the other samples. Its inverse relationship with activity was previously reported for several materials, ferrierite and Li- and Cs-exchanged ferrierite among them [5]. It can be considered that the presence of tungsten either on the surface or in the framework does not generate active sites selective to the butene skeletal isomerization, influencing all reactions. Exchanged samples attain higher isobutene yields, as shown in table 2. $W_{H1}KF$ produces practically two times the isobutene yield corresponding to AF. W/HF shows a low isobutene yield at a long TOS, even though this material presents strong acid sites. Considering the tungsten addition on the protonic form allows the formation of active sites with a modified environment and/or with another density, plus the difference in species reducibility, it would show a different surface when the carbonaceous deposit is formed.

Table 2
Isobutene yield for different samples. TOS: 120–140 min.

Sample	$W_{H1}KF$	$W_{L2}AF$	$W_{L1}KF$	$W_{L2}KF$	W/AF	AF	W/HF	W/KF	KF
Yield (%)	26.6	21.9	21.5	18.2	14.9	13.5	6.8	3.1	0.1

Figure 4 displays by-product distributions for different samples. At 5 min (figure 4(A)), the largest by-product proportion corresponds to the C_5^+ fraction, following propane, propene, and *n*-butane in similar proportions. W/KF presents a different behavior between all samples with the largest propene proportion and practically without propane, *n*-butane being lower and the C_5^+ fraction slightly larger. This sample does not have strong acid sites [9]. At a long TOS (figure 4(B)), AF and the tungsten-containing KF samples produce a propene proportion similar to or slightly lower than the corresponding C_5^+ fraction, whereas propene is higher than the C_5^+ fraction for the tungsten-containing AF samples. Butane and similar proportions of propane and ethane follow in decreasing order. $W_{H1}KF$ presents a distribution pattern similar to the corresponding AF; W/KF and W/HF produce the largest ethene proportion. Finally, the effect of TOS over the by-product distribution for a characteristic sample is shown in figure 5. The large increase in propene and the decrease of both propane and C_5^+ fraction are the main changes.

The reaction mechanism during the linear butene isomerization on ferrierite remains under discussion. On fresh ferrierite, non-selective material, it is proposed that the reaction occurs through either a bimolecular mechanism [24,25] or a monomolecular one [3,26], being the by-products formed on different active sites [26]. Evidence of a substantial amount of isobutene formed *via* a non-selective bimolecular mechanism, together with by-products, was recently reported [27]. On the aged catalyst, it is generally accepted that the bimolecular mechanism cannot occur, whereas a monomolecular one can take place [24,27,28]. A pseudo-monomolecular mechanism was also reported in order

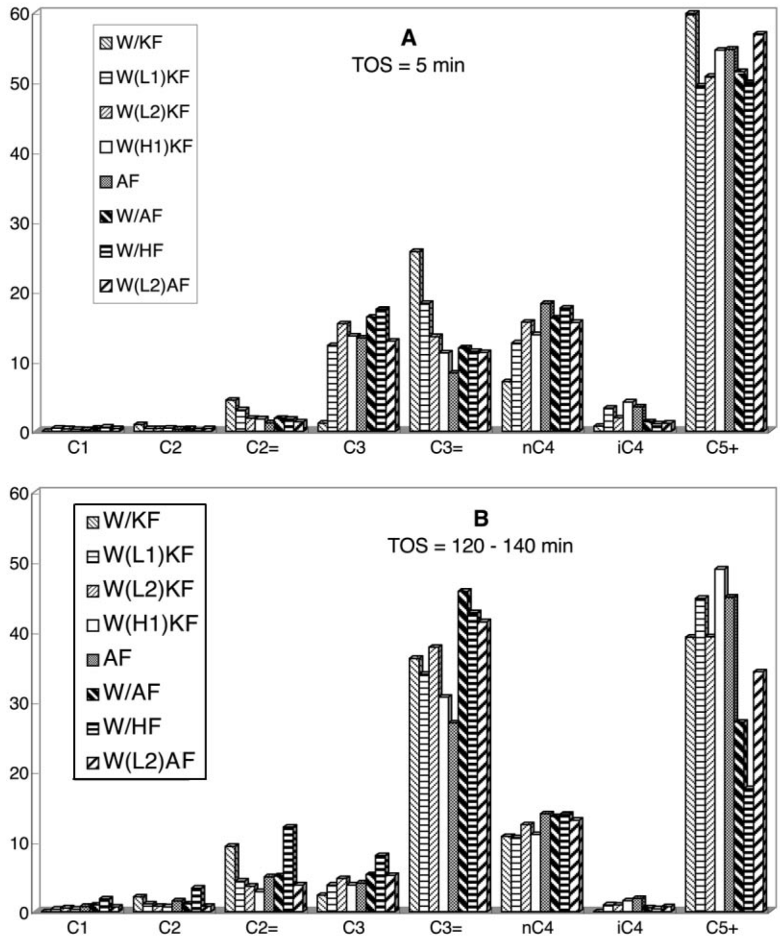

Figure 4. By-product distributions (mol%) at 5 min (A) and 120–140 min (B) corresponding to the 1-butene reaction on different samples. Activity test at 300 °C, 1 atm, and 0.15 atm 1-butene partial pressure.

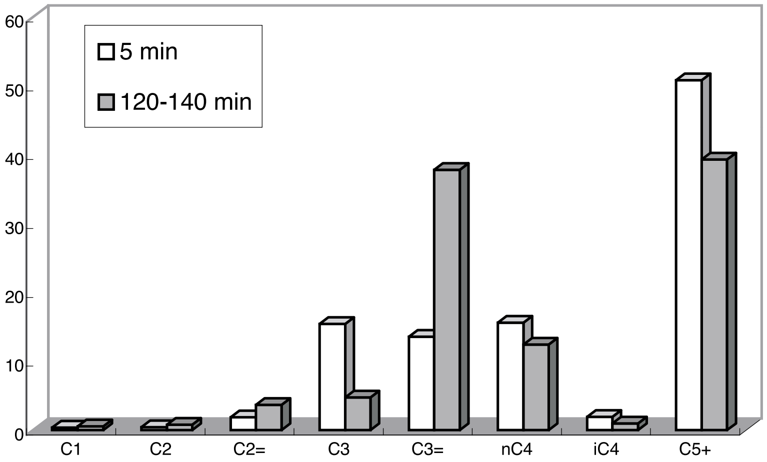

Figure 5. Effect of TOS over the by-product distribution (mol%) corresponding to the 1-butene reaction on a characteristic sample. Activity test at 300 °C, 1 atm, and 0.15 atm 1-butene partial pressure.

to explain the catalytic behavior of ferrierite [29]. By analyzing previous by-product distributions, the practically negligible C_1 and C_2 proportions allow one to consider the formation of dimers and/or oligomers. At 5 min, the C_5^+ fraction is larger than propane plus propene. When the surface still remains "clean", active sites and/or its environment being slightly modified, the high reactivity of propene favors its participation in other reactions. At a long TOS, the C_5^+ fraction is similar to propene. Therefore, when the largest amount of carbonaceous deposit is already formed, modifying the active sites and/or its environment, the bimolecular mechanism still takes place, thus explaining the by-product distribution.

4. Conclusions

Tungsten-ferrierite catalysts were prepared by impregnation following the incipient-wetness technique and by ion-exchange. Impregnated catalysts show reduction peaks characteristic of tungsten species in the TPR profiles. But the absence of peaks in the corresponding profiles of the exchanged material indicates such species were incorporated into the zeolite framework. For impregnated materials, the tungsten species–surface interaction is not strong.

During the linear butene skeletal isomerization, exchanged materials reach both conversion and isobutene yield larger than the impregnated ones. Samples prepared from AF and HF practically display the same catalytic behavior at 5 min, being associated with the presence of strong acid sites. W/KF shows a distinctive behavior, without a high activity at a short TOS and displaying a particular by-product distribution related to the absence of strong acid sites. Samples prepared by ion-exchange starting from KF show the HF characteristic behavior; differences at 5 min could be related either to a modified environment or to a different density of the strong acid sites generated. By-product distributions allow us to consider their formation from dimers and/or oligomers. At 5 min, the C_5^+ fraction is the main one, following propene, propane, and butane in similar proportions. Over the "clean" surface, propene could be involved in other reactions considering its high reactivity. At a long TOS, both the C_5^+ fraction and propane decrease, whereas propene increases, thus verifying the bimolecular mechanism.

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