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Isobutene production from skeletal isomerization of 1-butene on WO_x/ferrierite

Zunilda R. Finelli, Nora S. Fígoli and Raúl A. Comelli

Instituto de Investigaciones en Catálisis y Petroquímica – INCAPE (FIQ-UNL, CONICET), Santiago del Estero 2654, 3000 Santa Fe, Argentina
E-mail: rcomelli@fiqus.unl.edu.ar

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Both potassium and ammonium ferrierite (FK and FA, respectively) were impregnated with tungsten species using either tungstic acid or ammonium metatungstate as precursors. The skeletal isomerization of 1-butene at 200–400 °C, atmospheric pressure and 0.15 atm 1-butene partial pressure, was studied on samples with and without tungsten. Tungsten species on FK promote the isobutene formation while those species on FA generate a synergetic effect over the isobutene production. The presence of tungsten species improves the material stability and mainly, the isobutene yield. Starting the 1-butene feed over the catalytic bed at 200 °C and then increasing the reaction temperature to 400 °C, makes it possible to avoid the low isobutene selectivity at short times-on-stream.

Keywords: skeletal isomerization, n-butene, isobutene, ferrierite, tungsten species

1. Introduction

The skeletal isomerization of n-butenes is an attractive route for the production of isobutene, which is an important material to produce methyl *tert*-butyl ether currently used as a major booster of the octane number for reformulated gasolines. Zeolites, with both suitable acidity and pore size, achieve desirable activity and selectivity in this isomerization [1–5]; some authors consider that the pore structure plays a more important role than acidity in order to improve the isobutene selectivity [1,4]. More recently, the most suitable zeolitic materials for n-butene skeletal isomerization are those with pore diameter between 4.0 and 5.5 Å, which is the range shown by the 10-membered ring molecular sieves [6]. Ferrierite, a medium pore zeolite, is of current interest since it displays unique selectivity to isobutene [7]. Ferrierite [8] has an orthorhombic framework containing one-dimensional channels of ten-membered rings (4.2×5.4 Å) perpendicularly intersected by one-dimensional channels of eight-membered rings (3.5×4.8 Å). This pore structure system limits oligomerization and aromatization reactions while allowing the skeletal isomerization of n-butenes. However, initial selectivity to isobutene is low [9], and the catalyst displays better performance after some time-on-stream (TOS), when coke has been deposited. Seo et al. [10] showed that the deposited coke suppresses the dimerization–cracking process and thus leads to the enhancement of the selectivity to isobutene. This behavior has been related to the presence of two kinds of active acid sites [11]: selective and non-selective for skeletal isomerization. A monomolecular mechanism is proposed to occur over selective acid sites, a bimolecular mechanism taking place over non-selective sites [12]. Nevertheless, the n-butene skeletal isomerization mechanism still remains in discussion [13], and two possible mechanisms appear: monomolecular and bimolecular, the last one with some alternatives [14–16].

In their review, Butler and Nicolaides [17] showed that amorphous materials such as modified aluminas are active in n-butene skeletal isomerization. Among these materials, supported tungsten oxide (WO_x/Al_2O_3) allows both high activity and selectivity to isobutene [18–20]. These catalysts were usually prepared following an incipient wetness impregnation technique. Alumina without tungsten only shows activity in the double-bond shift isomerization with rapid deactivation when 1-butene is fed. After impregnation, the WO_x species promote skeletal isomerization activity, which is only achieved after a partial reduction of WO_3 [18]. The catalytic behavior has also been explained by considering the change of Lewis into Brønsted acid sites, rather than a change in total acidity [21].

In this paper we study the effect of WO_x species impregnation over ferrierite, in both potassium and ammonium forms, over the catalytic behavior during 1-butene skeletal isomerization. Furthermore, a practical way to diminish the formation of by-products at the beginning of the reaction, increasing the isobutene selectivity and avoiding the loss of raw material, is suggested.

2. Experimental

Potassium (FK) and ammonium (FA) ferrierite samples were provided by TOSOH, Japan (samples HSZ-720KOA and HSZ-720NHA, respectively). The SiO_2/Al_2O_3 molar ratio was 17.8; FA has Na_2O and K_2O contents lower than 0.05 and 0.10%, respectively.

Samples of FK and FA were impregnated with different tungsten loadings following the incipient wetness technique, using a volume of solution 10% larger than that corresponding to the pore volume. Tungstic acid and ammonium metatungstate were used as tungsten precursors. Solutions with the calculated concentrations to obtain a given tungsten loading on the solid were prepared. After impregnation, the samples were maintained for 4 h at room temperature, and then dried overnight in an oven at 110 °C. Samples were identified as $W_x(y)$/FK and $W_x(y)$/FA, x being the tungsten precursor used for impregnation ("a" for tungsten acid and "m" for ammonium metatungstate) and y the tungsten loading on the solid, expressed as weight percent referred to the dried base.

The crystalline structure of FK and FA was characterized by X-ray diffraction (XRD) using a Rich–Seifert Iso-Debyeflex 2002 diffractometer in the $0 < 2\theta < 60°$ range.

The catalytic behavior during the 1-butene skeletal isomerization was measured in a continuous flow fixed-bed quartz tubular reactor operated at atmospheric pressure, using 500 mg of catalyst sieved to 35–80 mesh. FK and FA were heated in a nitrogen stream (60 ml min^{-1}) from 25 to 550 °C in 30 min and held at this temperature for 30 min; tungsten containing samples were heated in a nitrogen (60 ml min^{-1}) plus air (50 ml min^{-1}) stream from 25 to 600 °C in 60 min and held at this temperature for 30 min. After heating, the samples were cooled to reaction temperature in a nitrogen stream. For tests at 400 °C, a pure 1-butene stream was co-fed with nitrogen for 180 min; for tests at different temperatures (200, 300, 380 and 400 °C), the pure 1-butene stream was co-fed starting at 200 °C and maintained for 40 min at each temperature. The reactants 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 isothermally at 100 °C. From these data, catalytic activity, selectivity to isobutene and isobutene yield, were calculated on a carbon basis. The catalytic activity is expressed as n-butene conversion. For this calculation, the three isomers of n-butenes are grouped together; this consideration is based on the fact that the isomerization of 1-butene to 2-butenes rapidly reaches equilibrium via double-bond migration, under reaction conditions.

3. Results and discussion

Figures 1 and 2 show the catalytic activity during n-butene skeletal isomerization and the selectivity to isobutene, respectively, at 400 °C, atmospheric pressure and 0.15 atm 1-butene partial pressure as a function of TOS, for FK and FA with and without tungsten. FK practically does not show activity (conversion lower than 1%). FA reaches a high conversion (≈75%) with low isobutene selectivity (≈20%) at short TOS; activity decreases and selectivity increases significantly during the first 40 min. W/FA samples display the same behavior with TOS; their activity is higher than the one obtained with the material without tungsten, the smallest tungsten loading reaching the best catalytic performance. W/FK samples do not show high activity values at short TOS (5 min) but show better stability; isobutene selectivity is higher than 55% for all samples. $W_a(3.0)$/FK presents the highest activity, reaching practically the same values as FA at TOS longer than 40 min. In general, the higher the activity, the lower the isobutene selectivity. At the same tungsten loading, FK and FA impregnated with tungstic acid present a slightly higher activity than when the precursor is ammonium metatungstate.

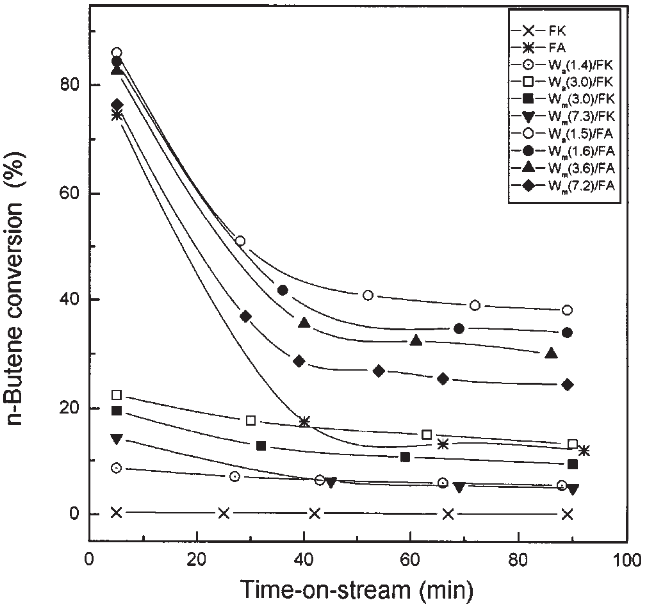

Figure 1. Catalytic activity (expressed as n-butene conversion) as a function of TOS for FK and FA with and without tungsten. Activity test at 400 °C, 1 atm, $p_{1\text{-}C_4^=} = 0.15$ atm, WHSV = 0.18 h^{-1}.

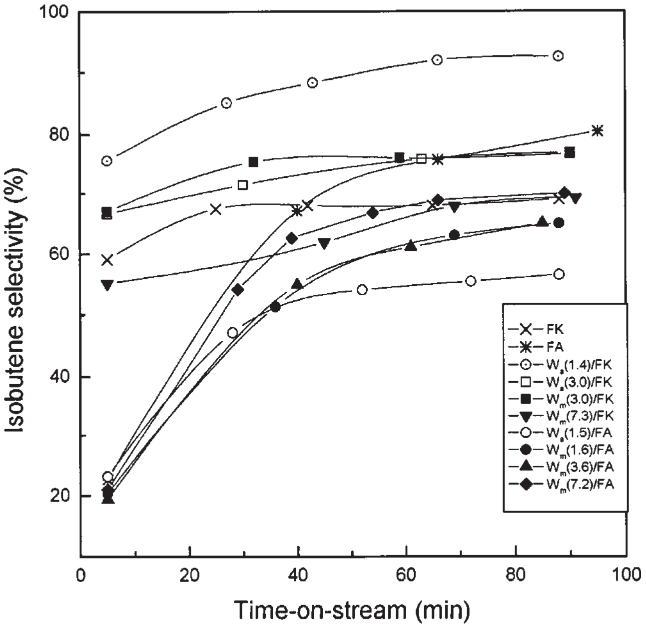

Figure 2. Selectivity to isobutene as a function of TOS for FK and FA with and without tungsten. Activity test at 400°C, 1 atm, $p_{1\text{-}C_4^=} = 0.15$ atm, WHSV = 0.18 h^{-1}.

Figure 3 shows the isobutene yield as a function of TOS for the former reaction conditions; significant differences are observed between the behavior of different samples. FK practically does not produce isobutene while FA presents a decrease in isobutene yield with TOS. W/FK samples also show a decrease with TOS; the qualitative behavior is similar to the activity, the 3.0% W loading makes it possible to obtain the best isobutene yield and using tungsten acid as precursor a small enhancement is observed. W$_a$(3.0)/FK reaches practically the same values as FA. W/FA samples present a distinctive behavior, the isobutene yield increases slightly at short TOS and then remains practically constant. Considering the tungsten loading, the sample with the lowest tungsten content shows the highest isobutene yield.

FK was practically inactive while FA presented activity during the n-butene skeletal isomerization, thus indicating that acidity is essential for catalytic activity, as has been previously reported [5]. We have exchanged FK samples with different ammonium hydroxide solutions (0.1–0.5–1.0–1.5 M), in one or two steps at room or at a higher temperature, in order to obtain different acidities. The sample exchanged with the 1.0 M solution gave the best catalytic performance, the same as FA. The tungsten species addition over FK promotes the activity and selectivity of the material, giving a good stability; it could be considered that WO$_x$ species generate acidity. Impregnating WO$_x$ species over FA, a synergetic effect is observed on both activity and isobutene yield, the latter maintaining its level with time. Soled et al. [21] reported that the addition of WO$_3$ on Al$_2$O$_3$ does not modify the total acidity of the material but changes the kind of acid sites, transforming Lewis into Brønsted acid sites, thus showing activity in the n-butene skeletal isomerization. Nevertheless, for the same catalytic system, Meijers et al. [20] reported that the presence of Brønsted acid sites is an important condition for n-butene skeletal isomerization, but the presence of W^{5+} ions (as Lewis acid sites) enhances the adsorption of butene, both types of sites being necessary. Some samples present particles with a blue color at the end of the reaction test; the amount increases with tungsten loading. Baker and Clark [18] reported that activity during the n-butene skeletal isomerization on WO$_x$/Al$_2$O$_3$ is only achieved after a partial reduction of the yellow WO$_3$ to a dark blue oxide; a number of intermediate oxides of tungsten are known, and the blue color of these oxides is reported [22]. Other reports also mentioned a similar chromatic effect during the partial reduction of WO$_3$ to yield hydrogen tungsten bronzes [23]. Consequently, it can be considered that WO$_x$ species present on ferrierite participate in the formation of partially reducible sites, which need either hydrogen or a reducing agent to generate the reduced form. The production of hydrogen during isomerization reactions, as a result of cracking of polymerized species, was previously reported [2]. Then, we can consider that the tungsten species added on ferrierite generate active sites for skeletal isomerization. Further study is necessary in order to relate the sites with acidity, adsorption and/or reduction properties.

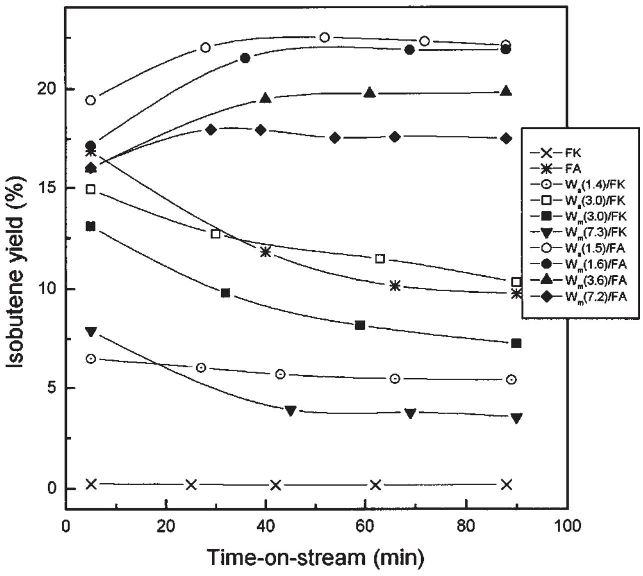

Figure 3. Isobutene yield as a function of TOS for FK and FA with and without tungsten. Activity test at 400 °C, 1 atm, $p_{1\text{-}C_4^=} = 0.15$ atm, WHSV $= 0.18\ \mathrm{h}^{-1}$.

FA presents a high n-butene conversion with a low isobutene selectivity at short TOS, then decreasing the ac-

Table 1

By-product yield during 1-butene skeletal isomerization on FK and FA with and without tungsten at 5 and 40 min.[a]

Sample	$C_1 + C_2$ (%)		C_3 (%)		n-C_4 (%)		i-C_4 (%)		C_5^+ (%)	
	5 min	40 min	5 min	40 min	5 min	40 min	5 min	40 min	5 min	40 min
FK	0	0	0.1	0.1	0.1	0	0	0	0.4	0.4
FA	0.8	0.2	10.3	2.8	7.6	1.2	1.7	<0.1	37.2	1.6
W$_a$(1.4)/FK	0	0	3.3	0.4	0.2	0.2	<0.1	0	0.8	0.2
W$_a$(3.0)/FK	<0.1	<0.1	2.3	1.9	1.3	1.2	0.4	<0.1	3.5	1.8
W$_m$(3.0)/FK	<0.1	<0.1	2.4	1.6	1.2	0.8	0.3	<0.1	2.6	0.7
W$_m$(7.3)/FK	1.8	<0.1	2.1	1.4	1.1	0.5	0.1	0	1.5	0.5
W$_a$(1.5)/FA	0.9	0.3	12.0	5.1	10.8	3.2	2.7	0.5	38.2	9.8
W$_m$(1.6)/FA	0.8	0.4	10.6	5.9	8.9	3.2	1.8	0.5	45.2	10.4
W$_m$(3.6)/FA	0.9	0.3	10.5	4.8	8.7	2.6	1.4	0.4	45.2	8.0
W$_m$(7.2)/FA	0.9	0.2	11.5	4.2	9.1	2.2	1.0	0.2	37.8	3.8

[a] Activity test at 400 °C, 1 atm, $p_{1\text{-}C_4^=} = 0.15$ atm, WHSV $= 0.18\ \mathrm{h}^{-1}$.

tivity and increasing the selectivity. This behavior has been explained by considering the existence of two types of active acid site [11]: internal ones (inside the zeolite pores) which are selective for skeletal isomerization, and external sites (on the external surface of the zeolite crystallites) which are non-selective for this reaction. A monomolecular reaction scheme takes place on selective sites while a bimolecular mechanism should occur on the non-selective sites [12]. The coke deposition during the first minutes is related to oligomerization and cracking reactions and the aromatization of these reaction products leads to the coverage of the external surface of crystallites, thus blocking pores and leading to slow overall deactivation [24]. The decrease in activity and increase in isobutene selectivity with TOS, for W/FA samples, similar to FA, and the isobutene yield practically constant, agree with the existence of two kinds of active sites previously reported, the non-selective ones which are deactivated during the first minutes and the selective ones which allow isobutene formation. The small increase in isobutene yield at short TOS could be related to the need of a partial reduction of the tungsten species involved in the isomerization process. A preliminary test was made using W$_{\text{m}}$(1.6)/FA pretreated in a gas stream of 5% hydrogen in nitrogen from 200 up to 400 °C during 1 h; after starting the 1-butene feed, the isobutene yield was maintained with TOS. This behavior agrees with the former idea. The absence of a significant decrease in activity at short TOS associated with a high isobutene selectivity and a slight decrease in isobutene yield, suggests that tungsten species on W/FK samples generate mainly selective active sites for the skeletal isomerization.

Table 2

Catalytic activity during 1-butene skeletal isomerization (expressed as n-butene conversion, $X_{n\text{-C}_4^=}$) and isobutene yield ($Y_{i\text{-C}_4^=}$) on FK and FA with and without tungsten at different reaction temperatures and at 5 and 40 min.[a]

Sample	T (°C)	$X_{n\text{-C}_4^=}$ (%)		$Y_{i\text{-C}_4^=}$ (%)	
		5 min	40 min	5 min	40 min
FK	200	–	–	–	–
	300	0.1	0.1	<0.1	<0.1
	380	0.2	0.1	0.1	0.1
	400	0.2	0.2	0.1	0.1
FA	200	1.5	0.4	0.5	0.2
	300	4.1	2.7	3.1	2.4
	380	19.7	13.5	11.2	8.2
	400	16.3	11.5	10.9	9.1
W$_{\text{a}}$(1.4)/FK	200	0.1	0.1	<0.1	<0.1
	300	1.0	0.8	0.9	0.6
	380	3.0	2.7	2.5	2.5
	400	3.8	4.1	3.4	3.8
W$_{\text{a}}$(3.0)/FK	200	0.6	0.3	0.2	0.1
	300	2.8	1.4	1.8	1.0
	380	6.4	5.5	3.6	3.8
	400	7.6	8.5	5.5	6.5
W$_{\text{m}}$(3.0)/FK	200	0.3	0.1	0.1	<0.1
	300	1.5	0.7	0.9	0.4
	380	5.7	2.7	1.6	1.6
	400	4.4	4.4	2.4	3.0
W$_{\text{m}}$(7.3)/FK	200	0.2	0.1	<0.1	<0.1
	300	0.8	0.4	0.4	0.2
	380	2.1	1.4	0.7	0.7
	400	2.4	2.5	1.2	1.6
W$_{\text{a}}$(1.5)/FA	200	–	–	–	–
	300	7.1	3.4	4.2	2.8
	380	23.5	19.7	15.6	15.1
	400	24.7	22.1	19.0	19.1
W$_{\text{m}}$(1.6)/FA	200	0.8	0.3	0.4	0.2
	300	4.4	3.3	3.3	2.9
	380	29.5	24.6	15.9	16.4
	400	35.1	31.3	20.6	20.5
W$_{\text{m}}$(3.6)/FA	200	–	–	–	–
	300	4.7	3.2	3.2	2.6
	380	26.6	22.3	14.4	14.6
	400	32.4	28.7	18.3	18.1
W$_{\text{m}}$(7.2)/FA	200	0.5	0.2	0.2	0.1
	300	3.6	2.1	2.2	1.8
	380	25.8	20.0	11.6	13.0
	400	28.0	25.4	17.3	17.4

[a] Activity test at 1 atm, $p_{1\text{-C}_4^=} = 0.15$ atm, WHSV $= 0.18\ \text{h}^{-1}$.

By-product yields corresponding to 400 °C at two TOS for different samples are shown in table 1. FK, which was practically inactive, only shows C_3 and C_5^+. W/FK samples present a similar behavior: practically, no C_1 and C_2, a larger proportion of C_3 (mainly propene) and C_5 (mainly pentenes) than C_4 and a small fraction of isobutane only at short TOS. FA, with and without tungsten, displays a similar behavior at short TOS: very few C_1 and C_2 (<1%), C_3 slightly higher than C_4, a higher proportion of isobutane (<3%) referred to FK samples, and a significant proportion of C_5^+. With increasing time, by-product yields decrease, the decrease in C_5^+ fraction on FA with and without tungsten being important. The absence of C_1 and C_2 between by-products suggests that the cracking process takes place from oligomers and not directly from C_4 species. The significant amount of C_5^+ on FA samples with and without tungsten also indicates the formation of oligomeric species. For these samples, the decrease in activity (mainly at short TOS) without important changes in the isobutene yield, supports the existence of two kinds of active sites, meanwhile the lower C_5^+ production at short TOS and the decrease in isobutene yield with time for W/FK could indicate the presence of only one type of active sites for the latter samples. The formation of butanes among by-products is evidence of hydrogen production, as previously reported [2]. The presence of isobutane at short TOS for FA with and without tungsten, may be understood by considering a hydrogen transfer reaction from isobutene and oligomeric species which deactivates non-selective active sites. For W/FK, the absence of isobutane could be explained by considering that the only type of active sites present does not favor hydrogen transfer reactions producing isobutene hydrogenation. For these samples, the by-product yield allows us to consider that metathesis can take place as previously reported over supported tungsten ox-

Table 3

Catalytic activity during 1-butene skeletal isomerization ($X_{n\text{-C}_4^=}$), selectivity to isobutene ($S_{i\text{-C}_4^=}$), and isobutene yield ($Y_{i\text{-C}_4^=}$) on FK and FA with and without tungsten at 5 and 40 min at 400 °C (reaction temperature).[a]

Sample	$X_{n\text{-C}_4^=}$ (%)				$S_{i\text{-C}_4^=}$ (%)				$Y_{i\text{-C}_4^=}$ (%)			
	$T_{\text{b}=400}$		$T_{\text{b}=200}$		$T_{\text{b}=400}$		$T_{\text{b}=200}$		$T_{\text{b}=400}$		$T_{\text{b}=200}$	
	5 min	40 min	5 min	40 min	5 min	40 min	5 min	40 min	5 min	40 min	5 min	40 min
FK	0.8	0.7	0.2	0.2	28.7	26.1	67.0	67.1	0.2	0.2	0.1	0.1
FA	74.5	17.6	16.3	11.6	22.6	67.1	66.9	79.0	16.9	11.8	10.9	9.1
W_a(1.4)/FK	10.7	6.4	3.8	4.1	59.2	88.3	90.6	92.7	6.3	5.7	3.4	3.8
W_a(3.0)/FK	22.4	17.8	7.6	8.5	66.6	71.5	72.2	76.5	14.9	12.7	5.5	6.5
W_m(3.0)/FK	19.5	13.0	4.4	4.4	67.0	75.4	54.2	68.3	13.1	9.8	2.4	3.0
W_m(7.3)/FK	14.4	6.3	2.4	2.5	55.2	61.9	49.4	64.0	7.9	3.9	1.2	1.6
W_a(1.5)/FA	84.0	48.7	24.7	22.1	23.1	47.1	76.7	86.4	19.4	22.9	19.0	19.1
W_m(1.6)/FA	84.4	41.9	35.1	31.3	20.4	51.3	58.7	65.4	17.2	21.5	20.6	20.5
W_m(3.6)/FA	82.6	35.6	32.4	28.7	19.3	54.8	56.5	62.9	16.0	19.5	18.3	18.0
W_m(7.2)/FA	76.4	28.7	28.0	25.4	21.0	62.6	61.6	68.4	16.0	18.0	17.3	17.4

[a] Activity test at 1 atm, $p_{1\text{-C}_4^=} = 0.15$ atm, WHSV $= 0.18$ h^{-1}, starting 1-butene feed either over the catalytic bed at 400°C ($T_{\text{b}=400}$) or over the bed at 200 °C ($T_{\text{b}=200}$) and then increasing temperature up to 400 °C.

ide [25]; moreover, a metathesis-like mechanism has been previously suggested for butene skeletal isomerization [26].

The catalytic behavior of FA and FK, with and without tungsten, was measured at 200, 300, 380 and 400 °C. Table 2 presents both activity and isobutene yield at those temperatures at 5 and 40 min. In general, the higher the reaction temperature, the higher the activity. The most important increment takes place between 300 and 380 °C. W_m(1.6)/FA reaches the highest activity (35.1%) at 400 °C and at 5 min. A slight decrease in activity with TOS is observed. By increasing reaction temperature the isobutene yield increases. At 200 °C isobutene is practically not formed; at 300 °C the yield is less than 4%. The isobutene production increases significantly at 380 °C, while the increase is smaller at 400 °C. The catalytic results at different reaction temperatures would allow us to consider that the presence of tungsten species does not modify significantly either the acidity or the type of acid sites.

A problem related to the use of ferrierite in the n-butene skeletal isomerization is the low isobutene selectivity at short TOS, considered as a loss of raw material. Table 3 displays n-butene conversion, selectivity to isobutene and isobutene yield at 400 °C, atmospheric pressure, 0.15 atm 1-butene partial pressure and at 5 and 40 min, when 1-butene is directly co-fed to the catalytic bed kept at 400 °C and when 1-butene is started and co-fed with the bed at 200 °C, then increasing the temperature up to 400 °C. Feeding 1-butene over the bed at 400 °C, the catalytic behavior observed is the one previously reported (high conversion with low isobutene selectivity at short TOS). Following the other procedure, the by-product fraction remains always low, reaching at 400 °C a high isobutene selectivity from short TOS, both n-butene conversion and isobutene yield being stable with TOS. For the last procedure, W/FA samples show at 400 °C and at short TOS (5 min) activity and isobutene yield levels which correspond to the stabilization values (at time longer than 40 min) when 1-butene is fed over the bed kept at 400 °C. Starting the reaction directly at 400 °C, at short TOS the non-selective active sites are responsible for oligomerization and cracking showing a high activity and diminishing the isobutene selectivity, which increases after a carbonaceous deposit is formed on those active sites, deactivating them. The presence of 1-butene while increasing the temperature of the bed from 200 to 400 °C also produces deactivation of the non-selective active sites, but without producing large amounts of by-products. Considering that n-butene double-bond shift isomerization is observed from the lowest temperature, the adsorption of reactant molecules on the active sites takes place; the low temperature favors oligomerization and polymerization rather than cracking of adsorbed species. Then, coke formation only allows the selective sites for skeletal isomerization to remain active when temperature reaches 400 °C. Deactivation tests using FA [27], in order to characterize coke formed at temperatures between 300 and 430 °C, showed large carbon contents under all reaction conditions (i.e., 7.1 and 9.2% for 300 and 400 °C, respectively) with significant differences in the temperature-programmed oxidation (TPO) profiles, suggesting changes mainly in the coke nature. In all cases, TPO profiles showed two peaks, one between 250 and 450 °C and another one between 550 and 700 °C; the peak at low temperatures is the main one when reaction takes place at 300 °C, while the peak at high temperatures is the largest when reaction was carried out at 400 °C. According to these results, it can be considered that at low reaction temperatures, the adsorption of species without high polymerization degree is favored, remaining on the surface and deactivating mainly the non-selective active sites for skeletal isomerization. A fast irreversible adsorption of butenes takes place at 350 °C, completely filling the micropores of ferrierite [24]. W/FK show lower activity and isobutene yield when the 1-butene is fed over the bed at 200 °C than when it is started directly at 400 °C, as can be seen in table 3. This agrees with our proposal presented above that only one type of active sites is present on the surface of these samples; when the adsorption of reactant molecules takes place, oligomerization occurs and coke formation deactivates the sites.

4. Conclusions

Addition of tungsten species on a material which does not show activity in the n-butene skeletal isomerization (FK) promotes isobutene formation while on a material (FA) with adequate acidity is active in that transformation and this generates a synergetic effect for isobutene production. The presence of tungsten species improves material stability, mainly isobutene yield. For FA with and without tungsten, starting the 1-butene feed over the catalytic bed at 200 °C and then increasing the temperature up to 400 °C prevents low isobutene selectivity at short TOS (avoiding loss of raw material).

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