Oxidative dehydrogenation of n-butane: a comparative study of thermal and catalytic reaction using Fe–Zn mixed oxides

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The thermal cracking of n-butane was compared with both thermal and catalytic n-butane oxidative dehydrogenation reactions. It was found that thermal oxidative dehydrogenation of n-butane was highly selective to n-butenes (approximately 70%) in the conversion range of 11–20%. This reaction proceeded at lower temperature than the thermal cracking of n-butane without oxygen. These results suggest that both reactions have different initiation steps. In the thermal cracking of n-butane the reaction initiated by the C–C bond scission, whereas for the thermal oxidative dehydrogenation of n-butane the removal of the hydrogen atom by the molecular oxygen to form $\dot{C}_4H_9$ and $H\dot{O}_2$ radicals was proposed as the main initiation step. On the other hand, butadiene was only obtained via a catalytic pathway, being strongly dependent on the reaction conditions.

Keywords: n-butane oxidative dehydrogenation, n-butane thermal cracking, iron–zinc mixed oxides

1. Introduction

The oxidative dehydrogenation process offers an alternative route for olefins and diolefins production with several advantages in comparison to the classical dehydrogenation process [1]. The oxidative dehydrogenation process represents a great potential commercial interest to utilize alkane effectively converting it to upgraded unsaturated hydrocarbons. However, catalytic oxidative dehydrogenation of alkanes is a complex process. This is accounted for by the low reactivity of the alkanes as well as by the presence of secondary competing reactions like thermal cracking and thermal oxidative dehydrogenation [2,3]. Oxidative dehydrogenation reactions have been the subject of several studies in recent years [4–7]. Most of them are focused to better understanding the activation mechanism of the C–H bond of lower alkanes (C_2–C_5) in the presence of molecular oxygen. Delmon et al. [8] pointed out that the interaction between the homogeneous and heterogeneous process must be taken seriously into account, if new processes in light alkane utilization are to be developed. The reasons are that: (1) some radical species can be generated in the gas phase, and/or (2) they can be also desorbed from the catalysts surface to the gas phase. Then, they could initiate homogeneous reactions in the pre- and/or post-catalytic zone [9,10].

Radical species as intermediates in the catalytic oxidation of hydrocarbons have been generally accepted [11,12]. Ismagilov et al. [9] reported that a branched chain oxidation reaction initiated by the surface may take place in the post-catalytic zone when n-propanol oxidation on $CuCr_2O_4/\gamma$-Al_2O_3 and Pt/γ-Al_2O_3 catalysts was carried out. Studying the propane oxidative dehydrogenation at 556 °C, Nguyen and Kung [10] showed the contribution of the thermal process developed in both pre- and post-catalytic zones. They proposed that propane conversion in the void volume immediately downstream of the catalytic bed was higher than that found in the same volume upstream of the catalytic bed. They also concluded that the main contribution to the propane conversion was the desorption of radical species from the catalyst, which gave rise to oxidative dehydrogenation of propane in the post-catalytic volume.

In this contribution a comparative study of the thermal cracking of n-butane with both thermal (without catalyst) and catalytic n-butane oxidative dehydrogenation reactions is presented. Information on the overall process of the thermal and catalytic n-butane oxidative dehydrogenation and on the mechanism of C–H bond activation by molecular oxygen is also attempted. The actual contribution of the catalysts to n-butenes and butadiene formation will be also analyzed. For the catalytic tests an iron–zinc mixed oxide was used [13].

2. Experimental

The n-butane oxidative dehydrogenation reaction was carried out in a conventional microreaction flow system operated at atmospheric pressure. Thermal cracking and thermal oxidative dehydrogenation of n-butane were evaluated in a Pyrex U-tube reactor and in a 16 cm^3 tubular reactor. For the catalytic oxidative dehydrogenation of n-butane a Pyrex porous plate was fixed into both types of reactor, in which the powdered catalyst was packed. The position of the Pyrex porous plate into the reactor gives rise to a pre-catalytic volume of 10 cm^3 and a post-catalytic volume of 6 cm^3. For the thermal cracking reactions a 60 cm^3/min flow of n-butane (Matheson C.P., 99%) was fed. For both the thermal and catalytic oxidative dehydrogenation reactions, a 60 cm^3/min flow of a mixture of n-butane, oxygen (Linde, 99.6%) and helium (Linde, 99.6%) was fed into the reactor. Typical flow ratio was $n\text{-}C_4 : O_2 : He = 2:1:2$. Throughout the study of the oxygen partial pressure effect, the mole fraction of n-butane was kept constant at 0.4 and the He flow was adjusted to keep a constant 60 cm^3/min total flow. The residence time was calculated dividing the volume of the heated reactor by the volumetric flow of the feed, measured at STP conditions. An iron–zinc mixed oxide, prepared in our laboratory with a $Fe/Zn = 5.8$ atomic ratio, was used as a catalyst [13]. The reaction products were analyzed on-line in a Varian Aerograph 3700 gas chromatograph equipped with a thermal conductivity detector and a 30 ft × 1/8 inch OD (23% SP-1700 on 80/100 chromosorb PAW) packed column.

3. Results and discussion

3.1. Thermal cracking

Thermal cracking of n-butane was carried out in the temperature range of 350–500 °C and a residence time of 16 s. The products distribution as a function of temperature is given in table 1. Propene and ethene were the products obtained. A propene/ethene molar ratio near to 2 was always obtained; hence, the α-breaking is favored over the β-breaking. At 350 °C the cracking reaction did not occur at all, whereas at 550 °C the n-butane conversion was 1.5 mol%.

3.2. Thermal oxidative dehydrogenation

Thermal oxidative dehydrogenation of n-butane was performed in the temperature range of 350–500 °C (at 325 °C there was no reaction at all) and a residence time ranging from 4 to 16 s. The pathway of n-butane thermal cracking changed when oxygen was added to the feed. The behavior of the thermal n-butane oxidative dehydrogenation as a function of temperature is shown in figure 1. The residence time was fixed at 16 s. Contrary to the n-butane cracking reaction, which showed activity above 400 °C, thermal oxidative dehydrogenation of n-butane showed already at 350 °C a conversion of 11% with a yield to n-butenes of 7.5% (68% selectivity). A small amount of CO_2 and traces of butadiene were obtained. Indeed, thermal oxidative dehydrogenation takes place at lower temperature than the oxygen-free cracking of n-butane. This behavior can be rationalized in terms of different initiation steps for each reaction. Given the high selectivity towards n-butenes, the thermal oxidative dehydrogenation initiates by the formation of butyl radicals generated by the interaction between n-butane and oxygen molecules. Thus, the main initiation step is the abstraction of a hydrogen atom from a butane molecule by the molecular oxygen to form $C_4H_9^\bullet$ and $HO_2^\bullet$ radicals. Notwithstanding, the mechanism through which molecular oxygen removes a hydrogen atom is still not well understood, due to the greater bond dissociation energy of the oxygen molecule compared with that of the C–C and C–H bonds.

Table 1
Thermal cracking of n-butane.[a]

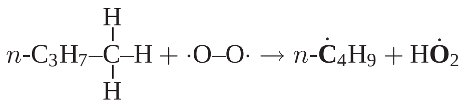
Temperature (°C)	Conversion (mol%)	Selectivity (mol%)		Propane/ethane ratio
		Propene	Ethene	
400	0.06	66.8	33.2	2.01
450	0.14	66.6	33.4	1.99
500	0.46	68.0	32.0	2.12
550	1.50	63.9	36.1	1.77

[a] Reaction conditions: residence time = 16 s, n-butane flow = 60 cm^3/min.

According to the molecular orbital theory [14] the electronic configuration of the oxygen molecule can be written as follows:

$$O_2 = KK\sigma_{2s}^2\sigma_{2s}^{*2}\sigma_{2p}^2\pi_{2p}^4\pi_{2p_y}^{*1}\pi_{2p_z}^{*1}.$$

It indicates that an oxygen molecule has two net bonds $(1\sigma, 1\pi)$ with an energy bond of 37 kcal/mol [14] and two unpaired electrons. If the bonds strengths pattern is considered, the formation of an ·O–O· type radical from molecular oxygen could be attained. Moreover, the two unpaired electrons give the oxygen molecule a biradical character. Therefore, this ·O–O· type radical could initiate a free-radical chain mechanism as follows:



$$n\text{-}C_3H_7\text{–}\overset{\displaystyle H}{\underset{\displaystyle H}{C}}\text{–}H + \cdot O\text{–}O\cdot \rightarrow n\text{-}\dot{\mathbf{C}}_4H_9 + H\dot{\mathbf{O}}_2$$

Once the formation of $n\text{-}\dot{\mathbf{C}}_4H_9$ radicals has been initiated, the reaction can then undergo a fast chain reaction with the oxygen remaining in the reaction medium. Taking into account the mechanism proposed by Baker et al. [15–17], the thermal n-butane oxidative dehydrogenation in the initiation and propagation steps can be summarized as follows:

(1) Initiation steps

$$n\text{-}C_4H_{10} + \cdot O\text{–}O\cdot \rightarrow n\text{-}\dot{\mathbf{C}}_4H_9 + H\dot{\mathbf{O}}_2$$
$$n\text{-}C_4H_{10} + H\dot{\mathbf{O}}_2 \rightarrow n\text{-}\dot{\mathbf{C}}_4H_9 + H_2O_2$$

(2) Propagation steps

$$n\text{-}\dot{\mathbf{C}}_4H_9 + O_2 \rightarrow 1\text{-}C_4H_8 + H\dot{\mathbf{O}}_2$$
$$n\text{-}\dot{\mathbf{C}}_4H_9 \rightarrow s\text{-}\dot{\mathbf{C}}_4H_9$$
$$s\text{-}\dot{\mathbf{C}}_4H_9 + O_2 \rightarrow 1\text{-}C_4H_8 + H\dot{\mathbf{O}}_2$$
$$H_2O_2 + \text{reactor's surface} \rightarrow 2\dot{\mathbf{O}}H + \text{reactor's surface}$$
$$n\text{-}C_4H_{10} + \dot{\mathbf{O}}H \rightarrow n\text{-}\dot{\mathbf{C}}_4H_9 + H_2O$$

The above general mechanism explains the main products distribution obtained in this study. In fact, Baker et al. [15,16] have proposed a detailed mechanism for olefins, cracking and combustion products formation by studying the effect of a small amount of n-butane addition

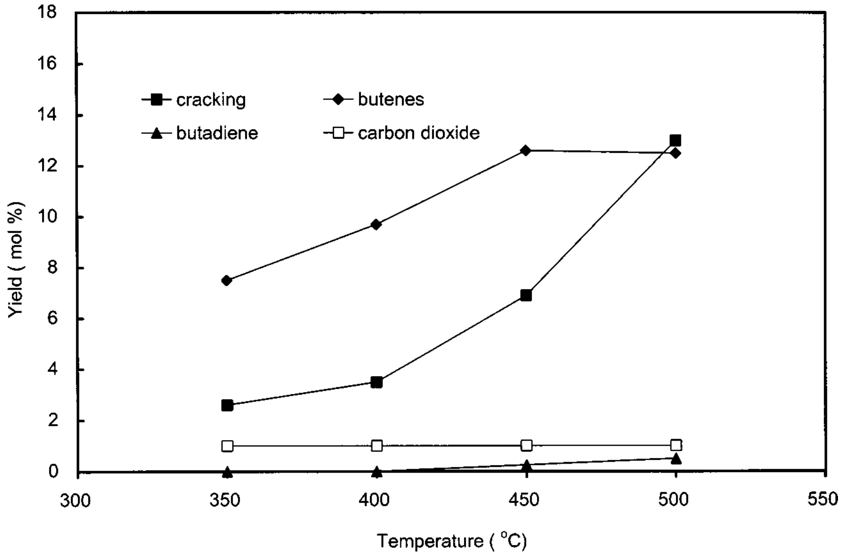


Figure 1. Effect of the reaction temperature in the thermal oxidative dehydrogenation of n-butane. Flow ratio $n\text{-C}_4:\text{O}_2:\text{He} = 2:1:2$, residence time $(\tau) = 16$ s.

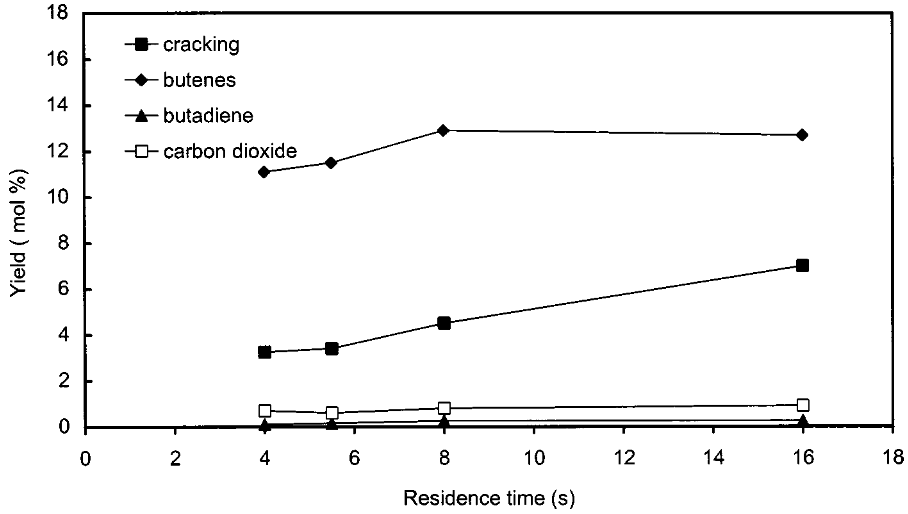
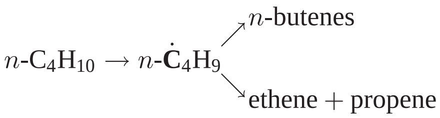


Figure 2. Effect of the residence time in the thermal oxidative dehydrogenation of n-butane. Flow rate = 60 cm^3/min, flow ratio $n\text{-C}_4:\text{O}_2:\text{He} = 2:1:2$, reaction temperature = 450 °C.

to the reacting mixture of H_2, O_2 and N_2 at 400 °C. They concluded that both olefins and cracking products could be formed from $n\text{-}\dot{\text{C}}_4\text{H}_9$ radicals via the $\text{H}\dot{\text{O}}_2$ radicals. However, the abstraction of the hydrogen atom from n-butane by oxygen was not clearly specified. The products distribution obtained in our study was similar to that obtained by Baker et al. [16,17].

It can be also observed in figure 1 that the yield of cracking products increased as the reaction temperature rose. Whereas, the yield to n-butenes remained constant in the range of temperature of 450–500 °C. Therefore, the global reaction pathway can be represented as a competitive scheme:



$$n\text{-C}_4\text{H}_{10} \rightarrow n\text{-}\dot{\text{C}}_4\text{H}_9 \begin{cases} \nearrow n\text{-butenes} \\ \searrow \text{ethene} + \text{propene} \end{cases}$$

Cracking products involve the rupture of a C–C bond, therefore, they are thermodynamically favored at higher temperature (endothermic reaction).

The effect of the residence time on the n-butane thermal oxidative dehydrogenation is plotted in figure 2. The yield to the cracking products increased as the residence time rose, whereas those to the n-butenes, CO_2 and butadiene were practically unaffected. These results can be explained assuming that butenes are formed by a fast chain reaction between the very reactive butyl radicals and oxygen. Such interaction generates more radicals, which increase the rate of the butenes formation. Hence, in the conditions used in this study, the butenes formation is not dependent on the residence time. Considering that cracking products are formed by a slower pyrolysis reaction, its yield increased as the residence time increased.

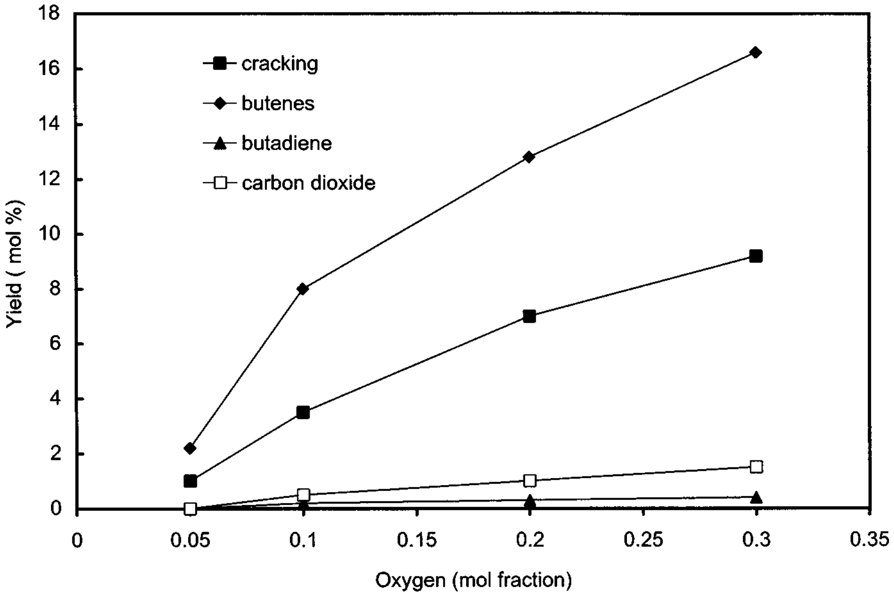


Figure 3. Effect of the oxygen partial pressure in the thermal oxidative dehydrogenation of n-butane. Flow rate = 60 cm^3/min, n-butane partial pressure = 0.4, reaction temperature = 450 °C, residence time = 16 s.

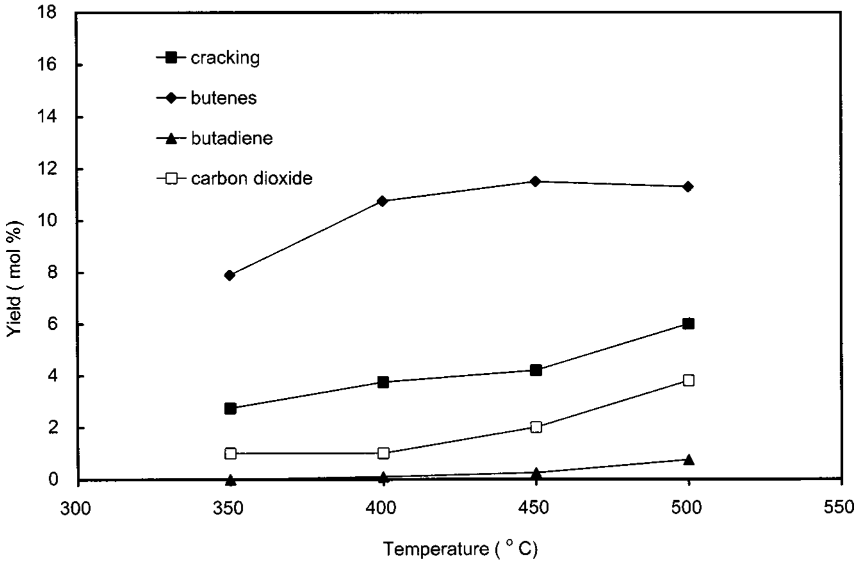


Figure 4. Influence of the reaction temperature in the catalytic oxidative dehydrogenation of n-butane. Flow rate = 60 cm^3/min, flow ratio n-$C_4 : O_2 : He = 2 : 1 : 2$, catalyst Fe–Zn–O, atomic ratio Fe/Zn = 5.8, weight of catalyst = 0.2 g.

The effect of the oxygen partial pressure was evaluated at 450 °C, and a residence time of 16 s, varying the oxygen mole fraction from 0.05 to 0.3. The n-butane mole fraction was kept constant at 0.4. As expected, the conversion increased as oxygen partial pressure increased (see figure 3). The yield to n-butenes was preferentially increased over the cracking products as the oxygen partial pressure rose. In addition, in all the thermal reactions only a small amount of butadiene was detected. This result indicates that the formation of two double bonds by a dehydrogenation reaction of n-butane via free radicals was not possible.

3.3. Catalytic oxidative dehydrogenation

Catalyst test was made at the same conditions as those for thermal oxidative dehydrogenation. Conversion and products yields are given in figure 4. Comparing these results with those obtained by thermal oxidative dehydrogenation (figure 1), it was found that at temperatures below 450 °C, the products distribution was very similar in both catalytic and non-catalytic reactions. However, at temperatures higher than 450 °C the yield to cracking products was lower and the yield to CO_2 was higher in the catalytic reaction than those of the thermal reaction. Whereas, the n-butenes yield was very similar in both thermal and

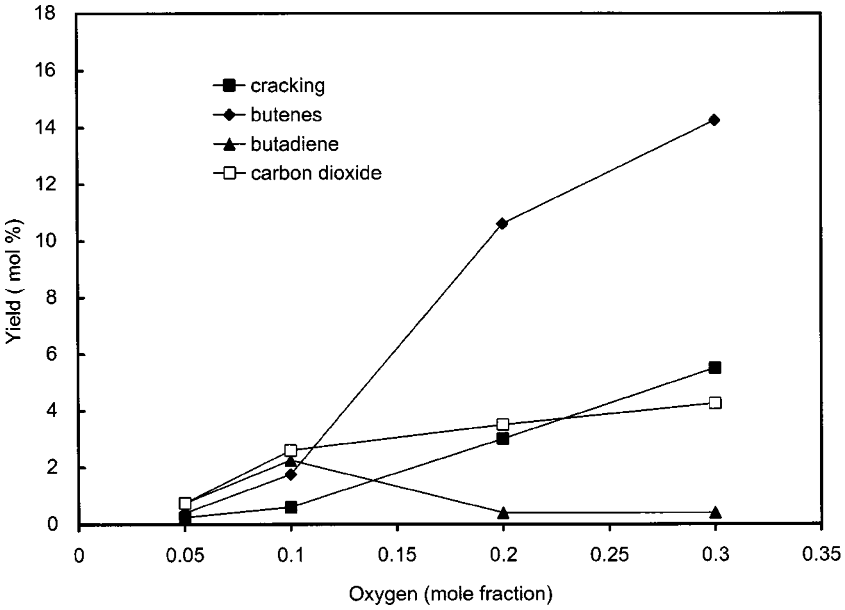


Figure 5. Influence of the oxygen partial pressure in the catalytic oxidative dehydrogenation of n-butane. Flow rate = 60 cm^3/min, n-butane partial pressure = 0.4, reaction temperature = 450 °C, catalyst Fe–Zn–O, atomic ratio Fe/Zn = 5.8, weight of catalyst = 0.2 g.

catalytic reactions. These results suggest that the catalyst did not affect the selectivity to dehydrogenation products. Nevertheless, these products were formed in the great void volume above the catalyst bed. It also indicates that these butenes do not react with the catalyst. Moreover, it could be concluded that in a catalyzed reaction, the combustion of cracking products is favored over butenes transformation.

The effect of the oxygen partial pressure in the catalytic oxidative dehydrogenation of n-butane was tested in a similar way to the thermal reaction and is shown in figure 5. When the mole fraction of oxygen is lower than 0.2, the conversion and yield to cracking products are lower than those in the absence of the catalyst. A considerable increase in butadiene formation was also observed. On the other hand, when the mole fraction of oxygen is higher than 0.1, the conversion and product distribution were similar to the thermal reaction. These results suggest that the catalytic dehydrogenation of n-butane could proceed in two ways depending on the reaction conditions. One is favored at higher oxygen partial pressure where the butenes formation proceeds by direct interaction with oxygen molecules in the homogeneous phase. Moreover, some of cracking products or their precursors are adsorbed on the catalyst and desorbed as CO_2. A second behavior is favored at lower oxygen partial pressure, in which n-butane is adsorbed on the catalyst and then transformed to butadiene. Figure 5 shows that butenes yield increases when the mole fraction of oxygen increases up to 0.1.

In tables 2 and 3 a direct comparison between the thermal and catalytic n-butane oxidative dehydrogenation is given. The tests were conducted using 0.2 and 2.0 g of catalyst. If the catalyst exerts any control over the dehydrogenation reaction, the extent of the catalytic reaction should increase when increasing the weight of the catalyst. Indeed, the yield to butadiene increases with the weight of the catalyst (see table 3). In addition, when the reaction conditions favor the thermal process (see table 2) an enhancement of the n-butane conversion was not observed.

Taking into account the last results and in order to find the conditions where the thermal contributions or the homogeneous reaction could be neglected, the reactor design was changed. The idea was to isolate the catalytic contribution. It seems that butadiene production arises via a catalytic pathway and it was favored at oxygen partial pressure of 0.1 (see figure 5). Then, at this flow ratio

Table 2
Oxidative dehydrogenation of n-butane at high oxygen mole fraction.[a]

Catalyst (g)	Conversion (mol%)	Yield (mol%)			
		Cracking	Butenes	Butadiene	CO_2
0.0	20.61	6.9	12.7	0.2	0.9
0.2	19.08	4.8	12.2	0.2	1.9
2.0	17.34	3.9	10.4	0.0	2.8

[a] Reaction conditions: flow ratio n-$C_4:O_2:He = 2:1:2$, temperature = 450 °C, n-butane partial pressure = 0.4, oxygen partial pressure = 0.2, catalyst Fe–Zn–O, atomic ratio Fe/Zn = 5.8.

Table 3
Oxidative dehydrogenation of n-butane at low oxygen mole fraction.[a]

Catalyst (g)	Conversion (mol%)	Yield (mol%)			
		Cracking	Butenes	Butadiene	CO_2
0.0[b]	3.1	0.7	2.4	0.0	0.0
0.2[b]	2.2	0.2	0.4	0.7	0.8
2.0[b]	3.8	0.3	0.9	1.1	1.5
0.2[c]	3.0	0.1	0.1	1.3	1.5

[a] Reaction conditions: flow ratio n-$C_4:O_2:He = 4:1:5$, temperature = 450 °C, n-butane partial pressure = 0.4, oxygen partial pressure = 0.05, catalyst Fe–Zn–O, atomic ratio Fe/Zn = 5.8.

[b] U-tube Pyrex reactor.

[c] Vertical tubular Pyrex reactor.

(n-$C_4 : O_2 : He = 4:1:5$) the thermal contribution to the oxidative dehydrogenation could be minimized in a Pyrex U-tube reactor. Then, these conditions were used in a Pyrex vertical tube reactor of 16 cm^3 (ID 0.9 cm × 20 cm). As expected, the thermal oxidative dehydrogenation did not proceed in this reactor (zero conversion was found). Hence, the catalytic oxidative dehydrogenation was tested here and the results are presented in table 3. Butadiene and CO_2 were the main products obtained when the oxidative dehydrogenation proceeded through a catalytic pathway. Therefore, n-butane oxidative dehydrogenation over a Fe–Zn–O mixed oxide catalyst proceeds all the way to butadiene and CO_2 formation, which means that Fe–Zn–O catalyst is able to develop a double dehydrogenation reaction in the n-butane molecule to produce butadiene.

4. Conclusions

Thermal oxidative dehydrogenation of n-butane proceeded at lower temperature than the oxygen-free thermal cracking of n-butane. Therefore, both reactions must have a different initiation step. For thermal n-butane oxidative dehydrogenation, the C–H bond scission by a biradical character of molecular oxygen is proposed as the main initiation step by the formation of butyl and HO_2 radicals.

Under our particular reaction conditions butadiene and CO_2 were only obtained via the catalytic pathway, which was strongly dependent on the reaction conditions. At higher oxygen partial pressure the thermal oxidative dehydrogenation was favored, and the reaction was mainly oriented to the n-butenes formation. In contrast, when the thermal and catalytic processes are operating, a mixture of n-butenes and butadiene must be expected in the reaction products.

The n-butane activation over a Fe–Zn–O mixed oxide catalyst proceeds up to the double dehydrogenation process yielding butadiene and CO_2 products. Whereas n-butane activation by molecular oxygen yields mainly n-butenes.

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