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Effect of carbon dioxide on the reaction performance of oxidative dehydrogenation of *n*-butane over V-Mg-O catalyst

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Abstract

Effect of carbon dioxide on the reaction performance of oxidative dehydrogenation of *n*-butane over vanadium-magnesium-oxides (V-Mg-O) catalyst was investigated using a conventional fixed-bed reactor. The catalyst characterization was carried out by XRD, TPD, TPR and BET technology. With the CO_2 partial pressure in the feed increases, the *n*-butane conversion decreases slightly but the selectivity and yield to C_4 dehydrogenation products increase. The selectivity to C_4 dehydrogenation products of up to 70.2% and yield of 34.1% were obtained by adding proper amount of CO_2 in the feed at 873 K. The high catalytic performance may be due to the competition between molecular O_2 and CO_2 adsorption on the active sites that are responsible for deep oxidation.

Keywords: Butane; Oxidative dehydrogenation; Carbon dioxide; Magnesium *ortho*-vanadate

1. Introduction

The demands of dienes and alkenes have increased tremendously throughout the world due to the vast growth of polymer industry. Oxidative dehydrogenation of lower alkanes (C_2–C_4) offers an alternation to thermal pyrolysis and catalytic dehydrogenation as a route for the production of alkenes. Oxidative dehydrogenation of alkanes is potentially much more economical since this reaction is exothermic and need not an external heat input, avoids equilibrium limitations. However, the alkanes and the desirable dehydrogenation products are easy to be deeply oxidized to carbon oxides (CO_x).

In the last decade, several research groups have been working on high active and selective catalysts for oxidative dehydrogenation of alkanes. Most catalysts described in the literatures are based on vanadium and molybdenum compounds supported or unsupported [1–7]. Vanadium-magnesium-oxides (V-Mg-O) are among the most selective and active catalysts for the oxidative dehydrogenation of *n*-butane to butene and butadiene [8], as well as of propane to propene [8–16].

The performance of V-Mg-O catalysts can be improved by using novel reactors or diluents. The inert membrane reactor (IMR) was found to be more efficient than a fixed-bed reactor for the oxidative dehydrogenation of *n*-butane under most of the conditions by Santamaria's group [17–19] and our own group [20]. Using Tellez's kinetic parameters [21], Assabumrungrat et al. have studied theoretically the oxidative dehydrogenation of *n*-butane in porous membrane reactors [22]. His model study showed that the membrane reactor outperformed the fixed bed reactor at high value of the air/*n*-butane ratio. Soler et al. studied a two-zone fluidized-bed reactor with separate butane and oxygen feeds in the oxidative dehydrogenation of butane and obtained higher selectivity and yield to the desired products, especially butadiene [23]. Later, Soler et al. proposed a mathematical model of the fluidized bed reactor to study its performance in the oxidative dehydrogenation of *n*-butane over V-Mg-O catalyst [24]. Lemonidou et al. reported that addition of water tended to decrease the conversion of butane and enhance the selectivity to dehydrogenation products [25]. But the selectivity and yield obtained in all literatures are too low to make the process commercially feasible.

Carbon dioxide is a kind of mild oxidant and can be used in the catalytic oxidation of alkanes. Oxidative dehydrogenation of ethane [26–28], propane [29], isobutene [29] and ethylbenzene [30–32] with carbon dioxide as an oxidant has been reported. Adding of CO_2 to the feed in the catalytic oxidation of alkanes to increase selectivity or yield to desired products has also been reported in literatures [33–37]. Liu et al. have reported that adding CO_2 to the partial oxidation of methane reaction made the temperature of hot sports

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in the catalyst bed to deduce significantly [33]. Moreover, Liu's results showed that adding CO_2 altered the H_2/CO ratio of the products. Zhaorigetu et al. have reported that an enhancement of the propene selectivity at isoconversion and thus of the propene yield was observed upon CO_2 addition on the feed in the oxidative dehydrogenation of propane [34]. Bi et al. have reported that selectivity to isobutene as well as isobutane conversion could be improved by adding CO_2 into the feed in the oxidative dehydrogenation of isobutane over LaBaSn oxide catalyst [35]. The favorable effect of adding CO_2 to the feed of reactors used for the oxidation of butane to maleic anhydride (MA) was reported by Santamaria's group [36,37]. A clear increases in the selectivity and yield to MA was observed upon addition of CO_2, using fixed-bed reactor [36] and membrane reactors [37].

In this paper, in order to improve selectivity and yield to C_4 dehydrogenation products (butene and butadiene) in the oxidative dehydrogenation of *n*-butane the influence of addition of CO_2 into the feed was investigated.

2. Experimental

2.1. Catalyst preparation and characterization

The catalyst preparation procedure was similar to one previously described [1]. The aqueous solution of magnesium nitrate was added to the aqueous solution of ammonium carbonate. The white precipitate was filtered, washed, dried and calcined. The resultant MgO was added to an aqueous solution containing 0.3 mol/l ammonium hydroxide and 0.4 mol/l ammonium vanadate at 343 K. The suspension was stirred and evaporated to dryness for 48 h. After the resulting solid was calcined at 823 K for 6 h. It was mixed with small amount of 1.0 mol/l HNO_3 and was extruded. Then it was calcined again at 823 K to decompose nitride. It was crushed and sieved to obtain a particle size between 0.25 and 0.42 mm. The catalyst contained 24 wt.% V_2O_5 and was termed 24-V-Mg-O.

BET specific surface areas were measured on a Micromeritics ASAP 2000 equipment using N_2 adsorption technology. X-ray diffraction (XRD) was performed on a Rijaku D/MAX2400 diffractometer equipped with Cu Kα radiation operated at 40 kV and 100 mA. Scan speed was 4°/min and scan step was 0.2°. Temperature-programmed reduction (TPR) results were obtained in a Shanghai 100 Instruments. Samples of 50 mg were first treated in air at 823 K for 1 h to disperse desorbed water, then the samples was cooled to room temperature. H_2/Ar mixture (H_2/Ar molar ratio of 1/9 and a total flow of 30 ml/min) was feed to samples and heated at a rate of 10 K/min, to a final temperature of 1000 K. The measurement process of temperature-programmed desorption (TPD) was similar to TPR, The samples of 50 mg were first treated in CO_2 (CO_2–TPD) at 823 K. Ar (Ar flow of 50 ml/min) was fed to the samples and heated at a rate of 10 K/min.

The used catalyst was prepared as follows: the reaction was carried out with 0.5 g of V-Mg-O catalyst for 12 h (reaction temperature of 873 K, total flow rate of 300 ml/min, molar ratio $n_{C_4H_{10}}/n_{O_2}/n_{N_2}$ of 4/8/88). After reaction only N_2 was fed to the catalyst and it was cooled quickly.

2.2. Catalyst tests

The catalytic reaction was carried out in a conventional flow system with a quartz tube reactor at close to atmospheric pressure. 24 V-Mg-O catalyst diluted by inert quartz chips was packed in the reactor and the other space was packed with quartz chips. 12 ml/min (all flows are given at STP conditions) butane was fed to the catalytic bed. The reaction temperature was varied between 793 and 873 K. An electric furnace maintained a constant temperature at the catalytic bed. The temperature values reported below referred to the set point of the furnace. Water was removed from the reactor effluents using ice trap. The incondensable gases were analyzed by on-line gas chromatography. Carbon balances were always better than ±5% and usually better than ±2% for the steady-state tests reported in this work.

3. Results and discussion

3.1. Catalyst characterization

Fig. 1 shows the XRD patterns of fresh and used V-Mg-O catalyst. Two crystal phases clearly identified were MgO and $Mg_3(VO_4)_2$. In addition, a trace of vanadium oxide (V_2O_5) was identified in the fresh catalyst. In the used catalyst, the crystal phase of V_2O_5 disappeared and the crystal phase of carbonates was not detected.

The surface area of fresh 24 V-Mg-O catalyst measured by BET technology was 52.0 m^2/g. The surface area of used catalyst was 51.0 m^2/g. The surface area was almost not decrease after reaction.

The TPR pattern of fresh catalyst shows two peaks (not shown in this paper). The first peaks started at 550 K and the

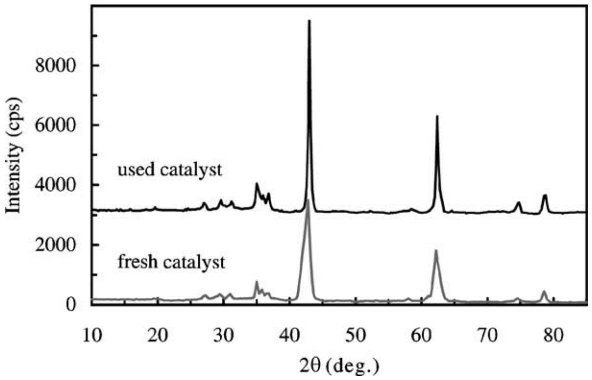

Fig. 1. The XRD patterns of fresh and used V-Mg-O catalyst.

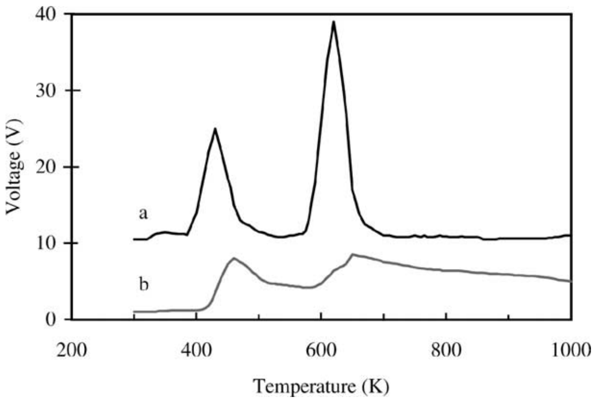

Fig. 2. The TPD pattern of fresh V-Mg-O catalyst (a) blank TPD, (b) CO$_2$–TPD.

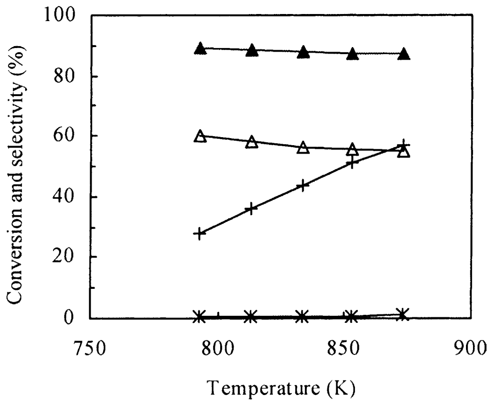

Fig. 3. Comparison of oxidative dehydrogenation with O$_2$ and dehydrogenation with CO$_2$. $W_{cat} = 0.5$ g, $n_{C_4H_{10}} = 4\%$, $F_{total} = 300$ ml/min. (+) $X_{C_4H_{10}}$–O$_2$; (△)S_{C_4}–O$_2$; (∗) $X_{C_4H_{10}}$–CO$_2$; (▲) S_{C_4}–CO$_2$.

second one started at 690 K. The two temperatures of the maximum hydrogenation consumption were 625 and 885 K respectively. According to Corma et al. [39] and Blasco et al. [5], the low temperature peak can be due to the reduction of isolated V^{5+} species in a distorted VO$_4$ tetrahedral environment on the catalyst surface and the high temperature peak can be due to isolated V^{5+} species in a Mg$_3$(VO$_4$)$_2$ structure in the bulk of the catalyst.

The nature of the V-Mg-O catalyst surface was tested by TPD of CO$_2$. Fig. 2 compares the blank and CO$_2$ TPD patterns. The blank (without CO$_2$ pretreatment) desorption curve showed two peaks due to the desorption of oxygen on the catalyst surface and thermal reduction of vanadium. The desorption curve of CO$_2$ also showed two peaks. Because there was not detector response observed below 373 K, the CO$_2$ physisorption on the surface of catalyst could be negligible. The first peaks started at 420 K and the top temperature was 460 K. The second one started at 600 K and the top temperature was 650 K. Even at high temperature 873 K, the detector response could be observed. The XRD result showed that crystal phase of carbonates was not detected, so the second peak found at high temperature should not be due to the decomposition of carbonates.

3.2. Oxidative dehydrogenation with O$_2$ and dehydrogenation with CO$_2$

Butene, butadiene, carbon oxides are the main products in the oxidative dehydrogenation of *n*-butane over V-Mg-O catalyst. Fig. 3 shows the comparison of oxidative dehydrogenation with O$_2$ and dehydrogenation with CO$_2$. Butane flow rate was kept at 12 ml/min. The molar ratio of $n_{C_4H_{10}}/n_{O_2}/n_{N_2}$ was 4/8/88 for oxidative dehydrogenation with oxygen. The molar ratio of $n_{C_4H_{10}}/n_{CO_2}/n_{N_2}$ was 4/30/66 for dehydrogenation with carbon dioxide. It can be seen that the activity of 24 V-Mg-O catalyst was very low in the dehydrogenation of *n*-butane when oxygen was in absence but CO$_2$ in presence in the feed. The selectivity to C$_4$ dehydrogenation products (S_{C_4}) was high for dehydrogenation of *n*-butane with CO$_2$. It can be observed that the selectivity to C$_4$ dehydrogenation products decreased with increasing reaction temperature from nearly 89.0% (temperature 793 K) to 85.2% (temperature 873 K). The activity of 24 V-Mg-O catalyst was very high in the oxidative dehydrogenation of *n*-butane with oxygen.

The oxidative dehydrogenation of *n*-butane over V-Mg-O catalyst is a complex parallel-consecutive reaction network. Butane reacts with lattice oxygen to create butene and butadiene. The activity and selectivity depend on the degree of reduction of the catalyst [8]. While the V-Mg-O catalyst is reduced by butane, it is very difficult to be reoxidized by CO$_2$.

3.3. Effect of CO$_2$ addition on the catalytic performance of V-Mg-O catalyst

In order to improve the selectivity to C$_4$ dehydrogenation products in the oxidative dehydrogenation of *n*-butane, the effect of addition of CO$_2$ in the feed on the catalytic behavior was studied. The stability of the catalytic performance for the oxidative dehydrogenation reaction in the presence of CO$_2$ in the feed was investigated. Fig. 4 shows the butane conversion ($X_{C_4H_{10}}$), selectivity and yield to C$_4$ dehydrogenation products (Y_{C_4}) as a function of time. It can be seen that the catalytic activity of V-Mg-O catalyst decreased, but the selectivity to C$_4$ dehydrogenation products increased slightly with time at first 2 h. Both the conversion and selectivity were approximately stable after 2 h. This is due to the stabilization of the oxidation state of the catalyst for a given set of reaction conditions. This two hours transient behavior was also observed by Tellez et al. using membrane reactor in the absence of CO$_2$ in the feed [17].

Fig. 5 compares the catalytic performance for the oxidative dehydrogenation of butane in the presence and absence of CO$_2$ in the feed. The molar ratio of $n_{C_4H_{10}}/n_{O_2}$ was kept constant at 4/6. CO$_2$ flux was kept at 90 ml/min ($n_{C_4H_{10}} =$ 30%) when CO$_2$ was added in the feed. The catalyst weight

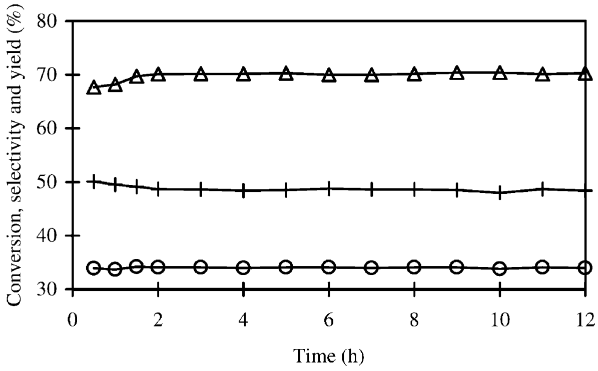

Fig. 4. Butane conversion, selectivity and yield to C_4 dehydrogenation products as a function of time in the presence of CO_2 in the feed ($W_{cat} = 0.5\,g$, $T = 873\,K$, $n_{C_4H_{10}}/n_{O_2}/n_{CO_2}/n_{N_2} = 4/6/30/60$ $F_{total} = 300\,ml/min$). (+) $X_{C_4H_{10}}$; (△) S_{C_4}; (○) Y_{C_4}.

was varied form 0.1 to 0.5 g. For the tested 24 V-Mg-O catalyst, an enhancement of the selectivity to C_4 dehydrogenation products at isoconversion and thus of the yield was observed with CO_2 addition in the feed.

Fig. 6 shows the effect of amount of CO_2 addition on the reaction performance in the oxidative dehydrogenation of *n*-butane over V-Mg-O catalyst. The CO_2 concentration was varied form 0 to 50%. N_2 was used as balance gas. It can be seen that the addition of CO_2 to the oxidative dehydrogenation reaction obviously increased the selectivity and yield to C_4 dehydrogenation products. Selectivities of CO and CO_2 decreased with increasing addition of CO_2 into the feed. While the CO_2 concentration was higher than 30% in the feed, the conversion and selectivity were almost constant.

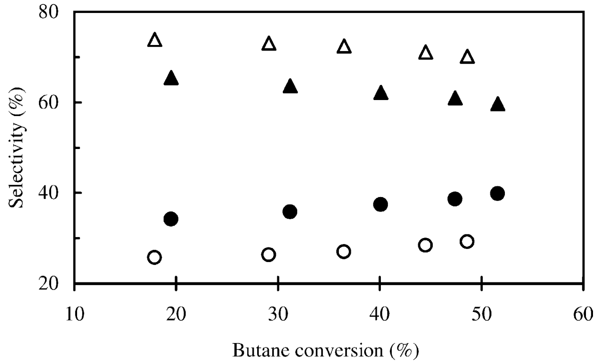

Fig. 5. Comparison of selectivity to C_4 dehydrogenation products and CO_x in the presence and absence of CO_2 in the feed ($W_{cat} = 0.5\,g$, $T = 873\,K$, $n_{C_4H_{10}}/n_{O_2} = 4/6$, $n_{C_4H_{10}} = 4\%$, $F_{total} = 300\,ml/min$). (△) S_{C_4}—addition of CO_2; (○) S_{CO_x}—addition of CO_2; (▲) S_{C_4}—without addition of CO_2; (●) S_{CO_x}—without addition of CO_2.

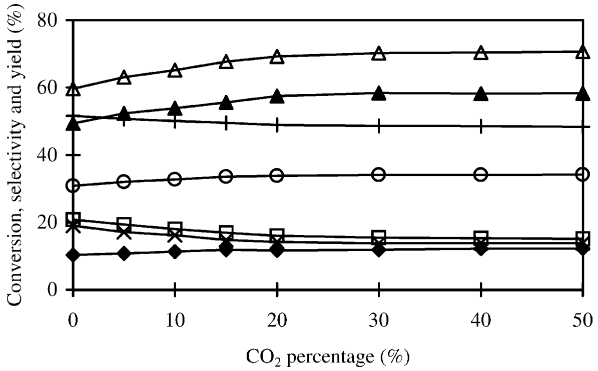

Fig. 6. Effect of amount of CO_2 addition on the reaction performance in the oxidative dehydrogenation of *n*-butane over V-Mg-O catalyst ($W_{cat} = 0.5\,g$, $T = 873\,K$, $n_{C_4H_{10}}/n_{O_2} = 4/6$, $F_{total} = 300\,ml/min$). (+) $X_{C_4H_{10}}$; (△) S_{C_4}; (▲) $S_{C_4H_6}$; (◆) $S_{C_4H_8}$; (○) Y_{C_4}; (□) S_{CO}; (×)S_{CO_2}.

There are several reasons that may contribute to the improvement of performance of the catalyst. On the reaction conditions, the surface composition of the working catalyst may change (e.g. alter the oxidation state of V species) and improve the catalytic performance. In addition, over V-Mg-O catalyst the oxidative dehydrogenation reactions consume lattice oxygen and the molecular oxygen adsorbed on the catalytic surface is believed to be responsible for the total oxidation of alkanes. Addition of CO_2 in the feed leads to the competition between molecular O_2 and CO_2 adsorption on the active sites and the decrease of the amount of adsorbed molecular O_2. Furthermore, CO_2 may poison the non-selective sites on the catalyst surface and result in the decrease of the deep oxidation. This possible explanation was reported before for the oxidation of butane to maleic anhydride over VPO catalyst [36,37] and the oxidative coupling of methane [38].

Fig. 7 shows the effect of reaction temperature on conversion, selectivities in the oxidative dehydrogenation of *n*-butane. These experiments were carried out with addition of 30% CO_2 in the feed. As the temperature increased from 793 to 873 K, butane conversion and the yield to C_4 dehydrogenation products increased, but the selectivity to C_4 dehydrogenation products and CO_x selectivity were almost constant. The results showed that the high temperature was beneficial to the formation of C_4 dehydrogenation products.

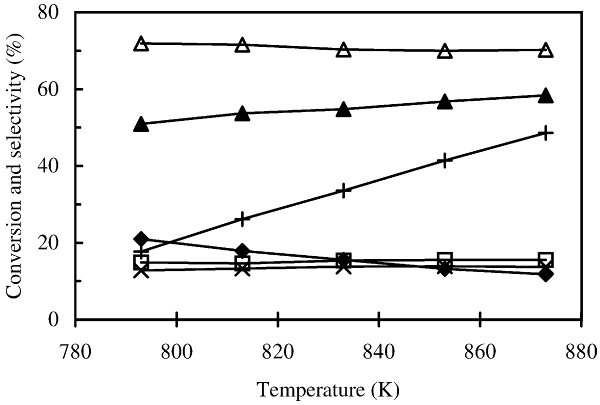

Fig. 7. Effect of reaction temperature on conversion and selectivities in the oxidative dehydrogenation of *n*-butane ($W_{cat} = 0.5\,g$, $n_{C_4H_{10}}/n_{O_2}/n_{CO_2}/n_{N_2} = 4/6/30/60$, $F_{total} = 300\,ml/min$). (+) $X_{C_4H_{10}}$; (△) S_{C_4}; (▲) $S_{C_4H_6}$; (◆) $S_{C_4H_8}$; (□) S_{CO}; (×) S_{CO_2}.

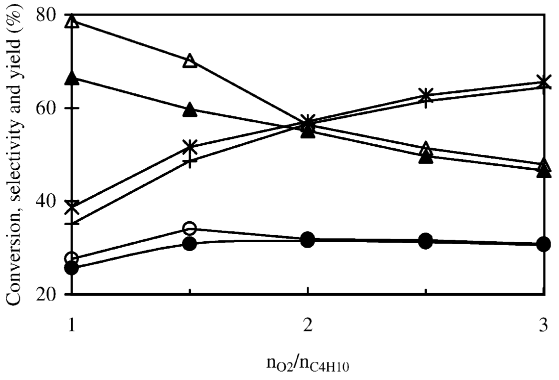

Fig. 8. Effect of molar ratio of $n_{O_2}/n_{C_4H_{10}}$ on conversion, selectivity and yield in the oxidative dehydrogenation of *n*-butane ($W_{cat} = 0.5$ g, $T = 873$ K, $n_{C_4H_{10}} = 4\%$, $F_{total} = 300$ ml/min, $n_{CO_2} = 30\%$ upon addition of CO_2). (+) $X_{C_4H_{10}}$—addition of CO_2; (△) S_{C_4}—addition of CO_2; (○) Y_{C_4}—addition of CO_2; (∗) $X_{C_4H_{10}}$—without addition of CO_2; (▲) S_{C_4}—without addition of CO_2; (●) Y_{C_4}—without addition of CO_2.

Oxygen partial pressure plays important role in the oxidative dehydrogenation of *n*-butane to butene and butadiene. Fig. 8 shows the effect of oxygen partial pressure on the catalytic performance. Butane flux and the total flux were kept constant at 12 and 300 ml/min, respectively. CO_2 flux was kept at 90 ml/min when CO_2 was added in the feed. For all the molar ratio of $n_{O_2}/n_{C_4H_{10}}$, addition of CO_2 in the feed could increase the selectivity and yield to C_4 dehydrogenation products. With increasing the value of $n_{O_2}/n_{C_4H_{10}}$, the butane conversion increased, but the selectivity to C_4 dehydrogenation products decreased. The different reactant composition has a strong influence on the performance of catalyst. The selectivity to C_4 dehydrogenation products varied from 78.7% (for $n_{O_2}/n_{C_4H_{10}} = 1.0$) to 47.9% (for $n_{O_2}/n_{C_4H_{10}} = 3.0$) when CO_2 was added into the feed. The improvement of the catalytic performance that is due to the addition of CO_2 in the feed decreased with increasing the oxygen partial pressure. The reason of this phenomenon is that the in situ reaction creates enough CO_2 at high oxygen partial pressure. The highest yield of 34.1% ($S_{C_4} = 70.2\%$) was obtained for $n_{O_2}/n_{C_4H_{10}}$ was 1.5 with 30% of CO_2 addition in the feed.

4. Conclusions

The oxidative dehydrogenation of *n*-butane over V-Mg-O catalyst can be successfully improved by addition of CO_2 in the feed. On the reaction conditions, the surface composition of the working catalyst may change and improve the catalytic performance. Addition of CO_2 in the feed leads to the competition between molecular O_2 and CO_2 adsorption on the surface of catalyst and the decrease of the amount adsorbed molecular O_2. Oxygen partial pressure plays important role in the oxidative dehydrogenation of *n*-butane to butene and butadiene in the absence or presence of CO_2 in the feed.

Acknowledgements

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