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Oxidative dehydrogenation of isobutane over LaBaSm oxide catalyst
Influence of the addition of CO_2 in the feed

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Abstract

Oxidative dehydrogenation (ODH) of isobutane over LaBaSm oxide catalyst in the temperature range 450–600°C, and the influence of the addition of CO_2 into the feed were investigated. It was found that LaBaSm oxide is an active and stable catalyst for ODH of isobutane. Upon reaction conditions the specific surface area decreases and a new phase, $La_2O(CO_3)_2$, is formed, which causes an increase in the surface specific conversion. The selectivity to isobutene as well as isobutane conversion can be improved by adding CO_2 into the feed. These effects may be explained as due to the combined effects of improvement of the active phase formation and the competition between molecular O_2 and CO_2 adsorption on the sites which are responsible for total oxidation. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Isobutane; Oxidative dehydrogenation; LaBaSm oxide catalyst; Isobutene; Carbon dioxide use in ODH

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1. Introduction

Isobutene has a particularly high demand as a feedstock in the production of oxygenated compounds such as methyl *t*-butyl ether (MTBE), as an additive to reformulated gasoline. Currently, isobutene is produced industrially by the endothermic dehydrogenation of isobutane over a Cr_2O_3–Al_2O_3 catalyst at 900 K [1]. In this process, carbon deposition leads to a rapid catalyst deactivation; consequently, periodic catalyst regeneration with air which result in evolution of a large amount of heat is required. Furthermore, the process is limited by thermodynamic constraints, and a large amount of heat is required. Therefore, researchers are pursuing ways to improve the isobutene yield, catalyst stability and process economics.

Oxidative dehydrogenation (ODH) of isobutane is potentially much more economical since this reaction is exothermic. However, as the formation of carbon oxides is thermodynamically more favourable than the formation of isobutene, the selectivity to isobutene decreases quickly with the increase in isobutane conversion, and the challenge is to improve the isobutene yield.

Compared to the ODH of other light alkanes (propane, ethane), the ODH of isobutane has received much less attention [2]. Takita et al. [3] studied the use of a number of metal pyrophosphates as catalysts for this reaction, and found that isobutene can be produced with 82% selectivity at 10% isobutane conversion over $Ni_2P_2O_7$ at 550°C. Cavani et al. [4] reported that Dawson-type $K_xP_2W_{17}MO_{62-y}$ (M=Fe, Mn,

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Co, Cu) catalysts showed good activity, and selectivities between 55 and 65% were obtained at isobutane conversion of 11–17%. Other types of mixed oxides [5–7] and supported transition metal oxides [8–10] have also been studied. The best catalytic performance at relatively low temperatures 200–300°C has been observed for chromium oxide supported on lanthanum carbonate [8] or on ceria [10].

Rare earth oxides or salts are known as suitable catalysts for light alkane conversion in the presence of oxygen [5,6,11–15], although the studies of their application to ODH of isobutane are scarce. Zhang et al. [5,6] have reported selectivities to isobutene up to 70% at 500°C over a number of rare earth catalysts promoted by cerium fluoride. The introduction of zirconium in the ceria network produces a significative improvement of the selectivity to isobutene of the pure ceria [13].

In a previous study, we found LaBaSm oxide is an active catalyst for the reaction of oxidative coupling methane (OCM) and most efficient among the LaBaM oxide series [16]. In this work, we have tried to extend this system to the ODH of isobutane. On the other hand, it has recently been reported that CO_2 can be used as a selective oxidant in the ODH of light alkanes over ceria [17]. In order to optimize the reaction feed composition to improve the isobutene selectivity, the influence of addition of CO_2 into feed has also been studied.

2. Experimental

2.1. Catalysts preparation and characterization

LaBaSm oxide catalyst was prepared by ceramic method. The stoichiometric amounts of La_2O_3, $Ba(OH)_2 \cdot 8H_2O$ and Sm_2O_3 (in atomic ratio La:Ba:Sm=2:1:0.03) were ground and mixed until a homogeneous mixture is obtained. It was calcined at 500°C for 2 h, and then at 1100°C for 6.5 h. After being stored under ambient conditions for certain time, prior to the catalytic tests, catalyst samples were pretreated in situ under air flow at 650°C for 2 h in order to have a reproducible initial surface state.

BET specific surface areas were measured on a Micromeritics ASAP 2000 equipment using N_2 adsorption at liquid nitrogen temperature. The XRD measurements were carried out at room temperature in a Seifert diffractometer system with Ni-filtered, Cu Kα radiation (λ=0.15406 nm), operated at 40 kV and 40 mA, using a 0.05° step size. The IR spectra were obtained on a Nicolet 5ZDX FT-IR spectrometer, provided with a MCTB detector. The samples were ground into fine powder and mixed with KBr to make a wafer containing 0.5–5 wt.% of catalyst sample, under a pressure of 5 t/cm^2. No other pretreatment of the sample was made, and the spectra were collected at room temperature with a resolution of 4 cm^{-1}.

2.2. Catalytic tests

The catalytic reaction was carried out in a conventional flow system equipped with a quartz reactor, using 0.5 g catalyst, and silicon carbide bits were filled in the void volume of the reactor bits. The feed composition was 10 ml/min isobutane, 0–5 ml/min O_2 and 0–15 ml/min CO_2 in helium. Total flow rate was 30 ml/min (all flows are given at STP conditions). The reaction temperature was varied between 450 and 600°C (or 650°C for dehydrogenation tests). The reaction products were analysed by an on-line gas chromatograph. A 4-m column packed with Porapak Q was used to separate the hydrocarbons, water and carbon dioxide, and a 1.5-m 13X molecular sieve column was used to separate oxygen and carbon monoxide. Conversion and selectivities are calculated on a C atom-basis and expressed as mol%.

3. Results and discussion

3.1. Catalytic activity

Catalytic performance data for the ODH of isobutane over LaBaSm oxide catalyst as a function of the reaction temperature are shown in Fig. 1. For comparison, the results of the catalytic dehydrogenation (DH) of isobutane (in the absence of oxygen) are also shown in this figure. In the absence of oxygen in the feed, at the initial stages of the run some carbon oxides were formed. Then, the products were isobutene propene and smaller amounts of C_1–C_2 hydrocarbons. It can be seen that the catalytic activity for DH was very low, becoming detectable at 500°C,

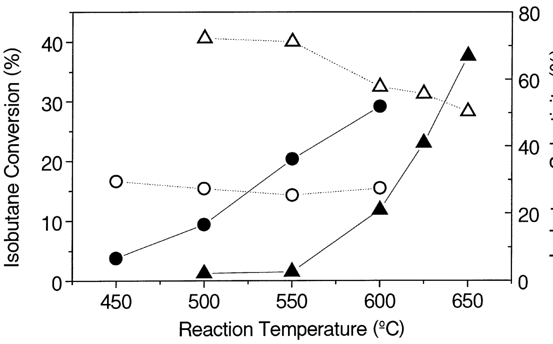

Fig. 1. Conversion of isobutane (filled symbols) and selectivity to isobutene (open symbols) as a function of reaction temperature in the catalytic ODH (circles) and DH (triangles) of isobutane over LaBaSm oxide catalyst. Reaction mixture: ODH, iC_4H_{10}:O_2:He=10:5:15 ml/min; DH, iC_4H_{10}:He=10:20 ml/min.

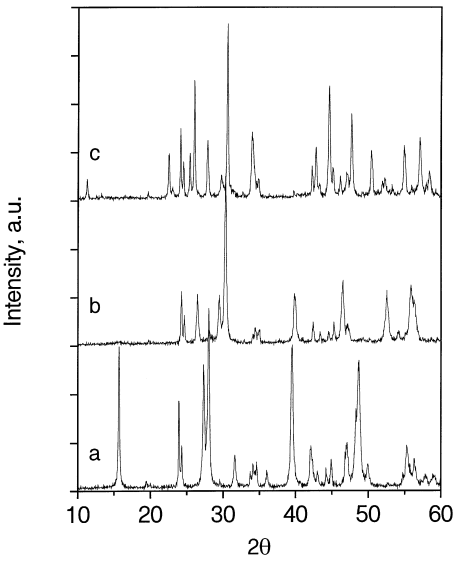

Fig. 2. XRD patterns of the LaBaSm oxide catalyst: (a) as prepared and stored under ambient conditions; (b) after treatment at 650°C in air for 2 h before reaction; and (c) after use in the isobutane ODH reaction.

while the selectivity to isobutene was high and decreased with temperature from nearly 70% to about 55%. As it could be expected, the catalytic activity for ODH (with oxygen in the feed) was much higher than that for DH: a conversion of 4% was already observed at 450°C, and 30% at 600°C. Also, the apparent activation energy was lower: 19.9±0.9 kcal/mol for ODH vs. 32.0±3.1 kcal/mol for DH. Isobutene, propene and carbon oxides (CO, CO_2) were the main products, while the amount of other trace products such as CH_4, C_2H_4 and $(CH_3)_2C{=}O$, etc. was negligible. However, the selectivity to isobutene of ODH is only about 27% in the whole range of reaction temperatures, and is much lower than that of DH.

3.2. Catalyst characterization

The XR diffractogram of the catalyst as prepared and stored under ambient conditions (Fig. 2a) shows a pattern which is in agreement with those reported in the literature for an aged-in-air lanthanum oxide [11,18], together with minor peaks corresponding to orthorhombic $BaCO_3$ (PDF 5-378) among which main peaks are at 2θ=24.0, 24.3 and 44.4° (d=3.72, 3.68, 2.05 Å). The main pattern is due to the evolution of lanthana upon exposure to air, which is well known for generation of partially carbonated hydroxide [18]. After treatment at 650°C for 2 h in air the diffractogram of the "fresh" catalyst (Fig. 2b) shows the peaks that may be ascribed to the hexagonal La_2O_3 phase (PDF 5-682, 2θ=30.3, 46.4, 39.8 and 55.9°) and the $BaCO_3$. No Sm-containing phase could be detected, probably either because the Sm content is very low or because their peaks overlap with those of the main lanthanum oxide phase. After the use of the catalyst in isobutane ODH reaction, its diffractogram (Fig. 2c) shows peaks corresponding to a new phase, hexagonal $La_2O_2CO_3$ (PDF 37-804), with main peaks at 2θ=30.4, 26.0 and 44.5° (d=2.94, 3.44 and 2.04 Å), as well as a strong decrease of the reflections of La_2O_3.

Similar trends were found by FT-IR spectroscopy. The spectrum of the catalyst as prepared and stored under ambient conditions (Fig. 3, bottom) shows intense, broad bands at 650, 1400–1500 and 3000–3600 cm^{-1} regions and sharp ones at 856 and 1750 cm^{-1}. It is similar to the IR spectrum of an aged-in-air lanthanum oxide reported by Bernal et al. [11], which shows the same bands at 650 and 3000–3600 cm^{-1} but much less intense bands at the 1400–1500 cm^{-1} region; this spectrum was interpreted in terms of the partial hydration and carbonation of the oxide in contact with atmospheric air. The main differences are due to a strong increase of intensity of the broad band 1400–1500 cm^{-1} and the sharp one at 856 cm^{-1}, characteristic of carbonates, both of which may be

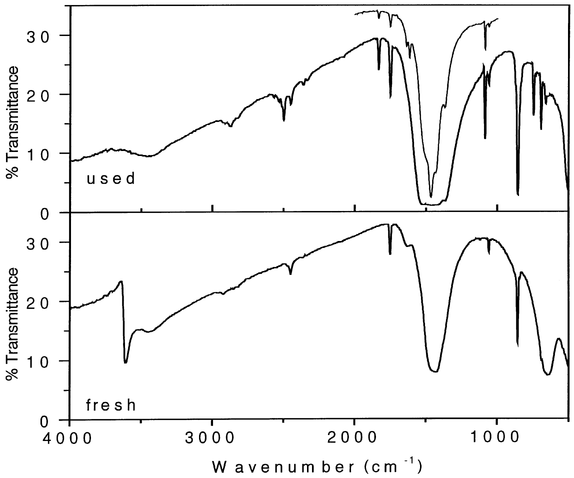

Fig. 3. FT-IR spectra of the LaBaSm oxide catalyst (5 wt.% in KBr) as prepared and stored under ambient conditions (fresh) and after use in the isobutane ODH reaction (used). The insert corresponds to the spectrum obtained using a sample with 0.5 wt.% catalyst content.

assigned to the spectrum of barium carbonate. This allows us to assume that the surface of the catalyst mostly consists of lanthanum oxide, partially hydrated and carbonated, and barium carbonate.

The spectrum of the catalyst after ODH reaction shows a very strong increase in the intensity of the bands at 856 and 1400–1500 cm^{-1} and the decrease of those at 3000–3600 cm^{-1}, while the band at 650 cm^{-1} (ascribed to lanthanum oxide) disappears and new, sharp bands appear at 693, 746, 1086 and 1834 cm^{-1}. A further analysis of the stronger band (insert in Fig. 3) showed the presence of shoulders at 1365 and 1465 cm^{-1}. All these new bands as well as the shoulders have been reported for the spectrum of $La_2O_2CO_3$ [11]. The appearance of these bands as well as the disappearance of the one at 640 cm^{-1} have also been observed in the spectrum of lanthanum oxide used in ODH of ethane, but no parallel carbonation phenomena could be observed over samarium oxide under the same reaction conditions [11]. It can be summarised that the IR spectra confirm the formation of the oxycarbonate phase during the ODH of isobutane, and indicates that the composition of the surface is similar to that of the bulk as shown by XRD data.

The BET surface area of the fresh catalyst was 4.1 m^2/g. However, this value decreased progressively with time in ODH reaction: it became 2.7 m^2/g after 40 h, 2.3 m^2/g after 70 h and 1.9 m^2/g after 120 h on stream.

3.3. *Catalytic properties stability*

The stability of the catalytic properties of LaBaSm oxide for the ODH reaction has also been studied. It was found that the catalytic activity of this catalyst decreased slightly with time (Table 1): conversion at the lower temperatures (500–550°C) dropped only around 30% after an accumulated reaction time of 120 h at 600°C. The apparently lower decrease (around 9%) observed at 600°C could probably be caused by the limitation of the total conversion by the exhaustion of the fed oxygen at this temperature. Further, no obvious coke could be found on the surface of the LaBaSm oxide catalyst after the reaction, which suggests that the carbon deposition can be inhibited by the presence of oxygen. A regeneration treatment of the catalyst with oxygen at 550°C for 1 h after 120 h on stream could recover only partially the activity (Table 1). Interestingly, the products distribution at each temperature remained practically unchanged in all cases, which suggests that the behaviour of LaBaSm oxide catalyst was very stable for this reaction.

As the specific surface area of LaBaSm oxide catalyst dropped gradually with the increase in reaction time (as discussed previously), this could be the reason for the decrease in activity. However, it should be noticed that this decrease in activity is much smaller than the decrease in the surface area (55% after 120 h on stream), which implies that the surface specific rate is *improving* with the reaction time. This could be related to the formation of the new monocarbonate-dioxide phase. In fact, Bernal et al. [11] found that the actual active phase in the ODH of ethane over lanthana is also $La_2O_2CO_3$ phase, that could be supporting our interpretation.

3.4. *Effect of CO_2 addition in the feed*

In order to improve this selectivity for ODH, we studied the effect of the addition of various amounts of CO_2 into the feed on the catalytic behaviour. The results are shown in Figs. 4 and 5. At the lower reaction temperatures (450 or 500°C), the conversion of

Table 1
The effect of reaction time on isobutane ODH over LaBaSm oxide and its BET surface area

Reaction time (h)	BET (m^2/g)	T (°C)	Conversion (%)		Selectivity (%)		Yield (%)	
			iC_4H_{10}	O_2	iC_4H_8	C_3H_6	iC_4H_8	C_3H_6
0 (Fresh catalyst)	4.1	500	9.4	70.2	27.3	17.0	2.6	1.6
		550	20.3	93.9	25.4	34.6	5.1	7.0
		600	29.0	99.1	27.4	38.2	8.0	11.2
120	1.9	500	6.6	52.6	26.4	17.3	1.7	1.1
		550	14.6	79.8	26.2	29.1	3.8	4.2
		600	26.7	93.9	29.0	36.4	7.7	9.7
120+1 h in O_2 flow	1.9	500	7.2	52.6	25.0	18.6	1.8	1.3
		550	16.0	80.7	26.0	33.2	4.2	5.3
		600	27.6	94.7	28.7	39.0	7.9	10.8

isobutane increased slightly when 5 or 10 ml/min CO_2 (equivalent to 16.6 and 33.3 mol%) were added into the feed, but a further increase up to 15 ml/min CO_2 caused its decrease (Fig. 4). This effect is much lower at 550°C and not observed at 600°C, although in the latter case it could be masked by the near complete conversion of oxygen, that could be limiting the total conversion. The amount of CO_2 added to the feed affects also the apparent activation energy. As it can be seen in Table 2, it decreased with the lower CO_2 content but increased for the higher CO_2 content.

At the same time, the selectivity to isobutene increased gradually with the increase of CO_2, and a substantial increase in selectivity to isobutene was observed when 15 ml/min CO_2 was added into the feed (Fig. 5, top). Besides, it can be seen that the selectivity to propene also increased obviously in the presence of CO_2 in the feed (Fig. 5, middle), while the selectivity to CO_x formed from isobutane decreased with the increase of CO_2 amount (Fig. 5, bottom). These results suggest that the isobutene selectivity for isobutane ODH may be significantly enhanced by adding a proper amount of CO_2 into the feed.

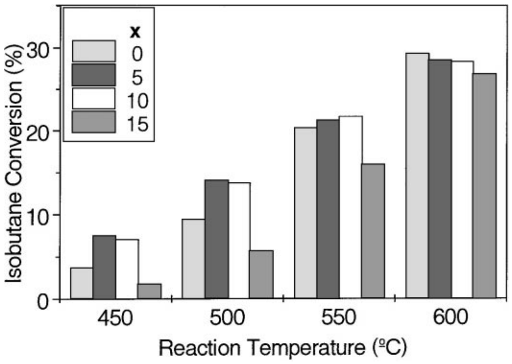

Fig. 4. Influence of CO_2 addition on the isobutane conversion as a function of temperature for ODH of isobutane over LaBaSm oxide catalyst. Feed composition: iC_4H_{10}:O_2:He:CO_2=10:5:(15−x):(x) ml/min.

The improvement of the selectivity to isobutene and the decrease in CO_x selectivity could be interpreted as due to the competition between the adsorption of molecular O_2 and CO_2 on the total oxidation sites of the catalyst. Similar results have been found in the ODH of propane over vanadates of rare earth elements by Zhaorigetu et al. [14]. They considered that, by addition of CO_2 into the feed, the adsorption–desorption equilibrium of CO_2 on the surface, probably on the basic oxidation sites, leads to a decrease in the amount of adsorbed molecular oxygen, which is believed to be responsible for the total oxidation of alkanes.

Table 2
Apparent activation energies of different reactions over LaBaSm oxide catalyst

Reaction	Catalyst (g)	Feed composition i C_4:O_2:CO_2:He	E_A (kcal/mol)[a]
DH	0.5	10:0:0:20	32.0±3.1
	0.5	10:0:15:5	34.7±6.6
ODH	0.5	10:5:0:15	19.9±0.9
	0.5	10:5:5:5	12.3±3.0
	0.5	10:5:10:10	13.8±3.4
	0.5	10:5:15:0	26.1±0.9

[a] Confidence interval for 95% probability.

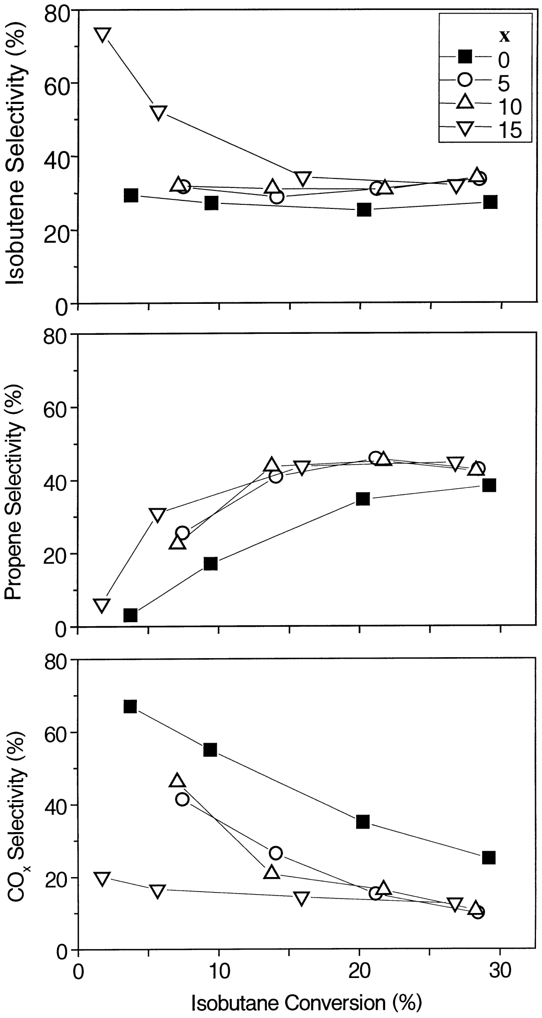

Fig. 5. Influence of CO_2 addition on the selectivity to isobutene (top), propene (middle) and CO_x (bottom) as a function of isobutane conversion in the ODH of isobutane over LaBaSm oxide catalyst. Reaction conditions as in Fig. 3.

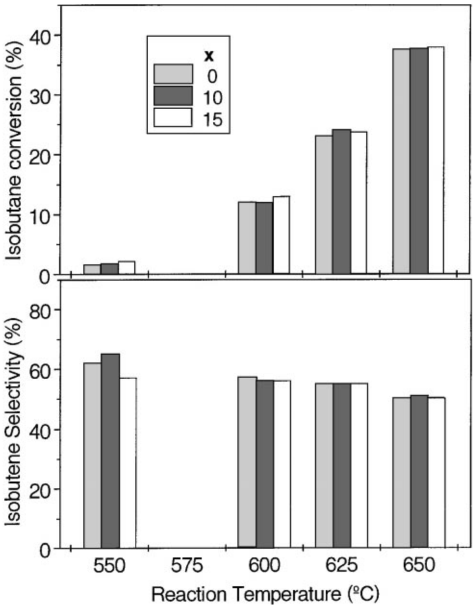

Fig. 6. Influence of CO_2 addition on isobutane conversion (top) and selectivity to isobutene (bottom) as a function of temperature in the dehydrogenation of isobutane over LaBaSm oxide catalyst in the presence of CO_2. Feed composition: iC_4H_{10}:He:CO_2=10:(15−x):(x) ml/min.

However, it is not very clear about how does CO_2 influence the conversion during the ODH reaction, and in particular how it may *increase* it. As some authors have found that CO_2 is a mild oxidant and can be used in the catalytic oxidation of alkanes over some types of catalysts [17,19,20], one of the possible reasons could be that CO_2 can react with isobutane directly. To check this possibility, the reaction of isobutane with different amounts of CO_2 over LaBaSm oxide catalyst in the absence of O_2 has also been studied, and compared with the DH results. As can be seen in Fig. 6, within experimental dispersion, both isobutane conversion and selectivity to isobutene remained at approximately the same level regardless of the different CO_2 content. This evidences that CO_2 may not react with isobutane directly under these reaction conditions.

Another possibility is that the addition of CO_2 modifies the nature of the active phase. Our XRD and IR spectra of the used catalyst show the presence of a new phase, $La_2O_2CO_3$, which is known to be active in ODH of alkanes, which was formed during ODH reaction tests. This phase may be formed by thermal decomposition of lanthanum carbonate [21]: the TPD of this phase shows two peaks, with maxima around 480 and 750°C, corresponding to the decomposition of the carbonate to the $La_2O_2CO_3$ phase and to the further decomposition of $La_2O_2CO_3$ to La_2O_3, respectively [22]. Thus, the oxycarbonate phase is stable in the temperature range used in our ODH. However, it is clear that its rate of formation, as well as the proportion between the lanthanum oxide, oxycarbonate and carbonate phases present in the surface of the catalyst under reaction conditions should depend on the partial pressure of CO_2 in the gas phase. Studies of isobutane ODH over chromia supported on lanthanum compounds have shown that the lanthanum carbonate is a more efficient catalyst component than the lanthanum oxide [8]. This could be indicative that the oxycarbonate (the actual phase in reaction conditions, as shown by TPD results) is more efficient for ODH than lanthanum oxide. This is further supported by our finding that the formation of the oxycarbonate phase during the ODH reaction is accompanied by an improvement of the surface specific activity. Therefore, one may assume that the observed trend caused by CO_2 addition (initial increase of conversion with a further decrease for higher CO_2 content, increase of selectivity to olefins) may be explained by the opposite effect of two phenomena: on one hand, the faster and more extended formation of the oxycarbonate phase which will cause the increase of the conversion, and on the other hand the inhibition of molecular oxygen adsorption by CO_2 adsorption (or inhibition of the adsorbed CO_2) which gives rise to the improvement in the selectivity to isobutene (and propene), and probably a decrease in the overall conversion in the case of the higher CO_2 content.

4. Conclusions

LaBaSm mixed oxides are active and stable catalysts for the oxidative dehydrogenation of isobutane into isobutene in the temperature range 450–600°C. Upon reaction conditions a new phase, $La_2O_2CO_3$, is formed which causes an improvement of the surface specific activity. The isobutene selectivity as well as the isobutane conversion at the lower temperatures (450–500°C) can be improved by addition of CO_2 into the feed. This influence of CO_2 can be attributed to a double effect: the faster formation of the more active oxycarbonate phase, and the competitive adsorption of molecular O_2 and CO_2 on the sites which are responsible for total oxidation.

Finally it should be noted that the use of CO_2 in the feed allows to obtain an overall selectivity to C_3–C_4 olefins between 55 and 80%, with combined yields up to 22%. This might be of practical interest and might provide an alternative to mild pyrolysis as a way to obtain light olefins from isobutane.

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