The influence of over-stoichiometry in $La_2Ni_{0.9}V_{0.1}O_{4.15+\delta}$ on selective oxidative dehydrogenation of propane

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## ABSTRACT

In this study, the non-stoichiometric redox compound $La_2Ni_{0.9}V_{0.1}O_{4.15+\delta}$ has been tested as an oxidant in selective oxidation of propane. The extent of over-stoichiometry (δ) was varied via both removing oxygen with propane in pulse experiments, as well as partial re-oxidation with oxygen. The optimal degree of over-stoichiometry (δ) has been quantified; olefins are formed whereas formation of CO_2 is prevented provided that δ is below 0.03. Additionally, the structural stability of the material was tested with in situ X-ray diffraction in H_2 (H_2-XRD), temperature programmed reduction (TPR), thermo-gravimetric analysis (TGA), propane-pulse-experiments and re-oxidation cycles. $La_2Ni_{0.9}V_{0.1}O_{4.15+\delta}$ has demonstrated structure stability at 550 °C and reversibility during oxidation–reduction cycles at 800 °C. Therefore, $La_2Ni_{0.9}V_{0.1}O_{4.15+\delta}$ is considered suitable for selective oxidative dehydrogenation of propane, provided that the degree of over-stoichiometry is limited to 0.03.

1. Introduction

The demand of propylene is expected to increase in the future because it is a crucial intermediate for many industrial processes [1]. The simplest and most direct way to obtain propylene is dehydrogenation of propane, as shown in Eq. (1).

$$C_3H_8 \leftrightarrows C_3H_6 + H_2 \quad \Delta H^\circ_{298} = +124\,kJ/mol \quad (1)$$
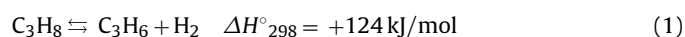
Catalytic dehydrogenation of propane using Cr- and Pt-supported catalysts was extensively studied in the past and several processes such as Catofin (from Houdry, United Catalyst Inc., ABB Lummus Crest), Oleflex (from UOP), Star (from Phillips Petroleum), FDB (from Snamprogetti) and PDH (from Linde-BASF) were commercialized [2]. Due to the high endothermicity of the reaction, high temperature is often required to increase the olefin yield. Unfortunately, operation at high temperature induces undesired cracking reactions, coke formation and consequent catalyst deactivation.

An alternative way for propylene production is oxidative dehydrogenation (ODH) of propane [3], as illustrated in Eq. (2).

$$C_3H_8 + O_2 \leftrightarrows C_3H_6 + H_2O \quad \Delta H^\circ_{298} = -118\,kJ/mol \quad (2)$$

The high quantity of heat generated by water formation turns the overall ODH of propane into an exothermic reaction, which overcomes the thermodynamic limitation. On the other hand, deep oxidation of propane to CO_2 is drastically decreasing the selectivity to olefins, due to the fact that highly reactive oxygen- and propyl-radicals are involved [4,5].

Many alternative oxidative agents were investigated (i.e. N_2O, H_2O_2 and CO_2) to accomplish less severe oxidative conditions, aiming at increasing the yield. It was shown [6] that replacing pure O_2 with N_2O/O_2 mixture in ammoxidation of propane over Fe-silicalite resulted in significant higher selectivity to acrylonitrile. Oxidation of propylene with H_2O_2 resulted in high selectivity to propylene oxide [7,8] and the same oxidative agent was also employed in selective oxidation of styrene to benzaldehyde [9]. CO_2 was also used as alternative oxidative agent on many reactions, i.e. ethylene production from ethane [10] and selective oxidation of ethylbenzene to styrene [11].

Another option to improve the selectivity is to use solid oxides as oxidant. Obviously, the oxide will be reduced when exposed to the hydrocarbons and the reactivity of the lattice oxygen depends on composition and structure of the oxide. After exposure to hydrocarbon, the oxide needs to be regenerated via oxidation. This scheme is rather similar to the classical Mars–Van Krevelen mechanism, with the difference that, in this case, the oxidation and reduction steps are separated. This separation can be made in *time*, using either moving bed technology or by switching between exposure to alkane and oxygen, respectively. This is the case of phthalic anhydride production from *o*-xylene, using VO_x/TiO_2 catalyst [12,13] or maleic anhydride production from *n*-butane over VPO catalyst

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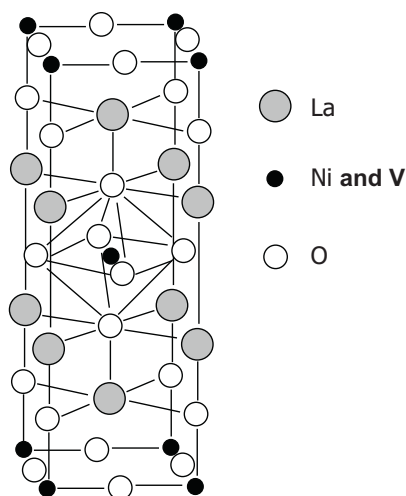
Fig. 1. Schematic representation of K_2NiF_4–structure related to $La_2Ni_{0.9}V_{0.1}O_{4.15+\delta}$ catalyst.

Fig. 2. Experimental mode scheme of sample pre-treatment and temperature programmed reduction in H_2 (RT–800 °C).

[14,15] in which double bed technology is required [16]. Alternatively, oxidation and reduction can be separated in *space* using a dense membrane reactor [17–23], performing oxidative conversion of the hydrocarbon at one side of the membrane, combined with diffusion of O^{2-} ions and electrons through the membrane and replenishing oxygen by exposing the other side of the membrane to molecular oxygen.

In this study, $La_2Ni_{0.9}V_{0.1}O_{4.15+\delta}$ oxide will be investigated as oxidant for selective oxidative dehydrogenation of propane, because of its favorable properties as oxygen conducting dense membrane [24,25]. $La_2Ni_{0.9}V_{0.1}O_{4.15+\delta}$ presents a K_2NiF_4-structure (perovskite-like structure) with a double layer arrangement: Ni and V, octahedrally coordinated, are present in the perovskite layer and La, tetragonally coordinated, is present in a rock-salt layer, as shown in Fig. 1.

Due to the specific crystallographic arrangement of this oxide and the redox nature of Ni and V, the oxide possesses two types of structural defects: vacancies and interstitial oxygen (indicated with δ in the catalyst nominal composition). Vacancies are lacking oxygen-ions in lattice position, like in many redox [26,27] and defective [28] compounds. Interstitial oxygen, typical for K_2NiF_4-structure materials, is due to the presence of over-stoichiometric oxygen which is located in between of perovskite and rock-salt layer, hence called interstitial oxygen (not shown in Fig. 1) [29]. As result, $La_2Ni_{0.9}V_{0.1}O_{4.15+\delta}$ contains two crystallographic types of oxygen ions (lattice and interstitial), possibly having different reactivity.

In our previous work [30] the role of over-stoichiometric oxygen as reactive species in selective oxidative dehydrogenation of propane over $La_2NiO_{4+\delta}$ and $La_2Ni_{0.9}V_{0.1}O_{4.15+\delta}$ was demonstrated via propane pulse experiments at 550 °C. It was shown that the depletion of oxygen and consequent decrease of reactivity affected the dominant reaction pathway. Slightly reduced oxide showed significant propylene formation, while CO_2 was the main product over oxidized material. Additionally, we reported that vanadium stabilizes the active oxygen active species, decreasing reactivity and enhancing the selectivity to propylene. Oxidative dehydrogenation is certainly not the exclusive reaction pathway as also cracking products (ethylene, methane) are observed [30], please note that we consider both propylene and ethylene as selective products. We have also shown [31] that varying the reaction temperatures between 450 and 650 °C influenced the product distribution drastically, which was attributed to the contribution different active species, i.e. interstitial oxygen, bulk oxygen and metallic Ni.
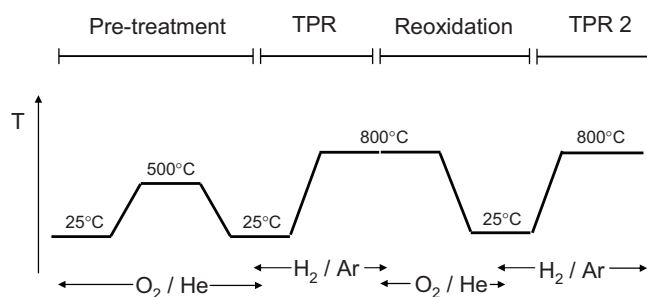
In this work we focused on conditions assuring that interstitial oxygen is the exclusive reactive species. The goal of this study is to quantify the relationship between the oxygen content of $La_2Ni_{0.9}V_{0.1}O_{4.15+\delta}$, i.e. the value of δ, and the reactivity with propane as well as the resulting selectivity pattern. Additionally, the structural stability of the material, the reactivity and the amount of over-stoichiometric oxygen when removing and re-absorbing those species, will be investigated.

2. Experimental

2.1. Catalyst preparation

The catalyst was prepared via sol–gel method using EDTA as chelating agent [30–32]. The appropriate amount of V_2O_5 (Merck) was dissolved in diluted HNO_3 (Merck) at 80 °C under stirring for 1 h. A stoichiometric amount of $La(NO_3)_3 \cdot 6H_2O$ (Merck), $Ni(NO_3)_2 \cdot 6H_2O$ (Merck), EDTA and NH_4OH solutions were added and the obtained solution was heated for 2 h under stirring.

After drying at 230 °C, foam-type material was formed and pyrolysis took place after spontaneous ignition. The resulting solid mixed metal oxide was milled and calcined in air, slowly increasing temperature (1 °C/min) up to 1050 °C to obtain pure phase materials. The resulting material was ball milled in acetone for 5 h and dried at 80 °C. The material was sieved and particles size of 0.1–0.3 mm (2.0 m^2/g) was used for all experiments.

2.2. Characterization

The crystal structure of fresh ∼0.5 mm thick pellet was studied with X-ray diffraction (XRD) using a Philips (X'Pert-MPD Pro) diffractometer with Cu Kα radiation (λ = 0.15406 nm). The pellet was fixed on the Pt sample holder by means of Ag-based glue. Data were collected varying 2θ between 20° and 80° with a step size of 0.01° and a step time of 10 s.

The XRD patterns of reduced sample were obtained after in situ reduction in H_2 in a high temperature chamber (Anton Paar HTK16). The temperature was increased up to 500 °C and 750 °C, respectively, in 4% H_2/Ar atmosphere and kept at those specific temperatures for 1 h. Subsequently, the samples were cooled down to room temperature under the same atmosphere and the XRD pattern was measured.

Temperature programmed reduction (TPR) was carried out with a home-built set-up, equipped with a TCD detector. First, 40 mg of sample mixed with 40 mg quartz particles were placed into a 4 mm inner diameter reactor, heated up to 500 °C (10 °C/min), kept at 500 °C for 1 h in a 20 ml/min flow of 5% O_2 in He and then the sample was cooled down to room temperature in the same atmosphere, as schematically presented in Fig. 2. At room temperature the flow was changed to 5% H_2 in Ar and the TPR was carried out at 5 °C/min up to 800 °C. Subsequently, after flushing the reactor with pure He
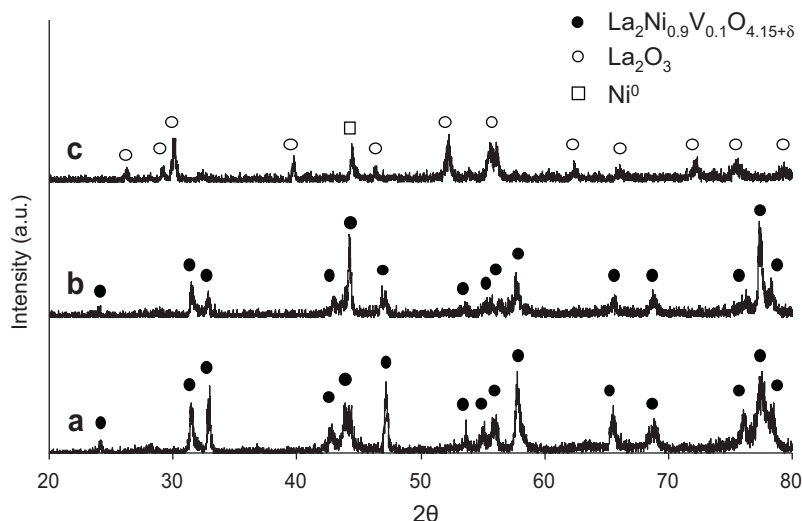
Fig. 3. In situ XRD pattern of fresh $La_2Ni_{0.9}V_{0.1}O_{4+\delta}$ (a), $La_2Ni_{0.9}V_{0.1}O_{4+\delta}$ reduced in H_2 at 500 °C (b) and $La_2Ni_{0.9}V_{0.1}O_{4+\delta}$ reduced in H_2 at 750 °C (c).

for 15 min, the flow was changed to 5%O_2 in He and the catalyst was re-oxidized for 1 h at 800 °C. The system was cooled down to room temperature under the same atmosphere and flushed with pure He for 15 min. Afterwards, the flow was changed to 5%H_2 in Ar and temperature was increased up to 800 °C and the reduction profile over re-oxidized sample was measured. The TCD was calibrated via reduction of NiO.

Thermal gravimetric analysis (TGA) was carried out using a Mettler-Toledo TGA-SDTA 851 unit. The sample (around 55 mg) was placed in a TGA cup and kept at 140 °C for 8 h to remove H_2O and any organic volatile compound adsorbed on the surface. Than the catalyst was heated up to 550 °C with rate of 10 °C/min in Ar flow of 40 ml/min. The weight loss was considered after 30 min of isothermal treatment at 550 °C, mimicking the pre-treatment of pulse experiment. To check the sample stability, the compound was kept at 550 °C for 14 h and the weight loss was considered. Experimental results were corrected for the buoyancy effect using a cup filled with quartz particles with similar volume.

2.3. Pulse experiment

Pulse experiments were carried out using a fix-bed reactor (quartz tube, length 400 mm, internal diameter 2 mm) at 550 °C. The catalyst particles (~35 mg) were sieved (particle size 0.1–0.3 mm) and packed between two quartz-wool plugs (length approximately 10 mm each). The remaining volume of the reactor was filled up with quartz particles, in order to reduce the void space and minimize gas phase reactions. Before each titration test, the catalysts were pre-treated in 10% of O_2 in He flow (20 ml/min, 30 min) at 720 °C in order to remove any trace of water or inorganic compounds physisorbed on surface and keep the catalyst oxygen level as high as possible. The samples were cooled down to reaction temperature under the same atmosphere, whereafter the gas flow was changed to He (3 ml/min). After flowing pure He for 15 min, pulses of 300 μl at atmospheric pressure containing 10% C_3H_8 in He were introduced, whereas pulses containing 10% O_2 in He were used to re-oxidize the catalyst, after exposure to C_3H_8 pulses.

Product distributions were monitored by sampling on-line to a quadrupole mass spectrometer (Pfeiffer AG Balzers, OmniStar) equipped with Channeltron and Faraday detectors (2–200 amu). Prior to each experiment, the fragmentation pattern of fresh propane and fresh oxygen were recorder and compared with the fragmentation pattern of the produced gas mixture to qualitatively

identify the products distribution. Water, propane, and oxygen were identified monitoring m/z = 18, 29 and, 32, respectively, since no other products contribute to those m/z signals significantly. To determine the presence of methane, ethane, ethylene, propylene and CO_2, two or three m/z signals were monitored for each compound. Because of the similarity in fragmentation patterns and the consequent contribution of several products to the same m/z signal (cross-contamination effect), matrix-type calculation was performed. In this way, formation of CO was also determined via m/z = 28, although many compounds as propane, ethylene and carbon dioxide also contribute to m/z = 28. These additional contributions were taken into account and subtracted from m/z = 28, resulting in apparent absence of CO, i.e. the CO concentration is blow the detection limit. The detection of H_2 was unfortunately not reliable. This procedure allows quantitative determination of propane and oxygen conversion only, with an experimental error of about 5%.

As the formation of products could not be quantified, only semi-quantitative comparison of selectivity patterns, called "apparent selectivity", will be reported. Apparent selectivities were calculated based on the integrated area of peaks of the corresponding m/z signals of each compound divided by total integrated areas of the peaks of all carbon containing products (e.g. for methane: $A(m/z_{CH_4})/A(m/z_{CH_4}) + A(m/z_{C_2H_6}) + A(m/z_{C_2H_4}) + A(m/z_{C_3H_6}) + A(m/z_{CO}) + A(m/z_{CO_2})$). The conversion of propane was below the detection limit when pulsing propane to the reactor filled with quartz particle exclusively and therefore we exclude gas phase initiation during the pulse tests. The amount of oxygen removed from the fresh catalyst during propane pulsing was quantified with help of back-titration with O_2.

In a second series of experiments, the oxidation state of the catalysts was manipulated by reoxidizing the catalyst partly, varying the number of O_2 pulses. Subsequently, propane pulse experiments were performed and the product distributions were compared.

3. Results

3.1. Characterization

Fig. 3 shows the influence of reduction in H_2 at 500 °C and at 750 °C on the XRD pattern of $La_2Ni_{0.9}V_{0.1}O_{4.15+\delta}$.

The fresh sample (Fig. 3a) possesses very good crystallinity and all peaks can be assigned to the K_2NiF_4 tetragonal structure, typical
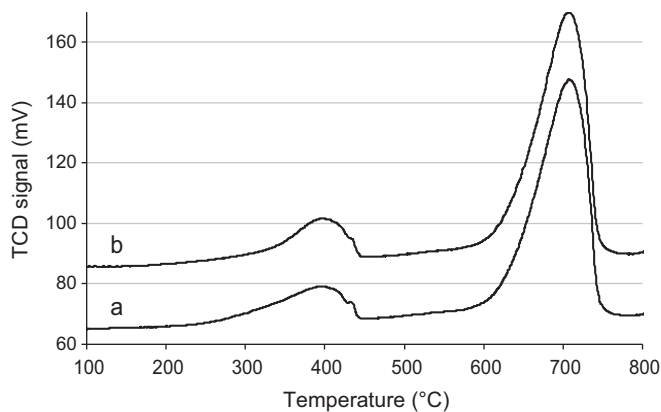
Fig. 4. Two consecutive temperature programmed reductions on fresh $La_2Ni_{0.9}V_{0.1}O_{4+\delta}$ (a) and on re-oxidized sample at 800 °C (b).

Fig. 6. Quantification of removed oxygen with back titration with O_2 after 1, 2, 3, 7, 12, 20 and 45 propane pulses along the pulse test on $La_2Ni_{0.9}V_{0.1}O_{4+\delta}$ at 550 °C.

for this type materials [33–36]. After reduction in H_2 at 500 °C (Fig. 3b) the intensity of most peaks decreases without changes in peak positions. Additionally, the two patterns clearly show different ratios in peak intensities in the range $31° < 2\theta < 33°$ as well as $42° < 2\theta < 48°$. Contrary, after reduction at 750 °C in H_2 the pattern changes completely (Fig. 3c), denoting the disappearance of the K_2NiF_4-type structure. All peaks observed in the new diffraction pattern can be assigned to La_2O_3 and Ni-metal. No peaks related to vanadium oxides were observed.

Temperature programmed reduction of fresh sample (Fig. 4a) resulted in two peaks with a maximum rate of H_2 consumption around 390 and 700 °C, which are typical for K_2NiF_4-type of materials [30,34,35]. The two reduction steps were already assigned in the literature to the removal of over-stoichiometric and lattice oxygen bonded to Ni^{2+} ions, respectively [30,31]. The observed reduction steps corresponded to removal of 0.41 ± 0.02 and 2.35 ± 0.1 mmol O/g of catalyst, respectively, in good agreement with quantification reported in the literature [30,31]. Fig. 4b confirms that re-oxidation of reduced catalyst restored the structure of the mixed oxide, based on the similarity of the TPR profiles of the fresh and re-oxidized catalysts.

Fig. 5 shows the thermal gravimetric analysis of fresh $La_2Ni_{0.9}V_{0.1}O_{4.15+\delta}$, resulting in weight loss of 0.231 mg between 200 and 550 °C, which corresponds to 0.26 mmol oxygen per gram of catalyst. The weight loss is associated with partial removal of over-stoichiometric oxygen as already reported in the literature for $La_2NiO_{4+\delta}$ [30,31,36]. The equilibration of catalyst weight at 550 °C occurred within 20–30 min. Moreover, subsequent isothermal treatment of 14 h at 550 °C caused an additional weight
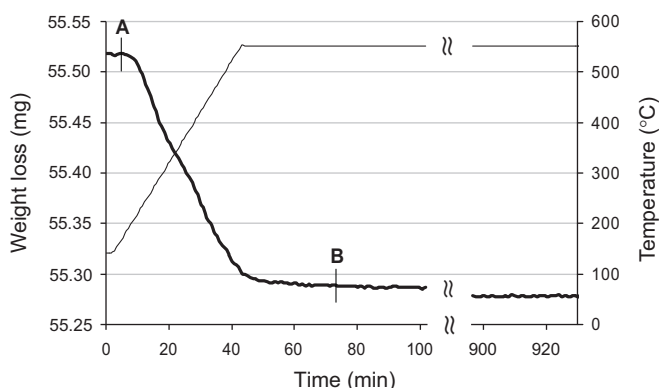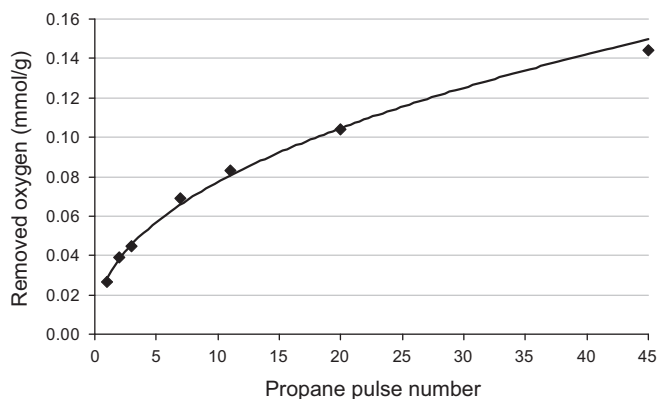
decrease equal to only 0.009 mg, i.e. less then 5% of the weight loss observed during the first 30 min.

3.2. Quantification of removed oxygen

The propane pulse test over fresh $La_2Ni_{0.9}V_{0.1}O_{4.15+\delta}$ at 550 °C was reported in our earlier paper [30]. As the results obtained here are essentially identical, the data are not repeated here and we focus on the results regarding quantification of the oxygen removed and regeneration of the oxide via re-oxidation.

Fig. 6 shows that the amount of removed oxygen, quantified with seven different back titrations with O_2, increases with the number of pulses; whereas the amount that is removed per pulse obviously decreases with decreasing oxygen content. After 45 pulses, 0.144 mmol oxygen per gram of catalyst was removed and the catalyst remained active (∼5% conversion).

Complete removal of the reactive oxygen was achieved by heating the catalyst in pure He from 25 to 550 °C and keeping the catalyst at 550 °C under diluted C_3H_8 atmosphere for 30 min, which resulted in subsequent zero C_3H_8 conversion. The back titration of removed oxygen at 550 °C resulted in 0.180 mmol/g in He atmosphere.

3.3. Products distribution of totally and partially oxidized catalysts

The propane conversion over completely oxidized $La_2Ni_{0.9}V_{0.1}O_{4.15+\delta}$ during pulse experiments at 550 °C (Fig. 7) showed a gradual decrease during the first 9 pulses of propane from 28% at the first pulse to 5% from the tenth pulse onwards,
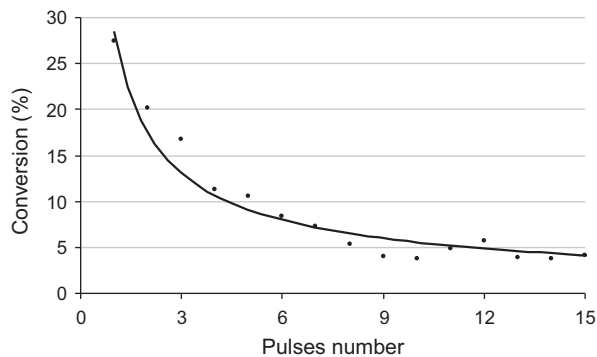

Fig. 5. Ar-TGA on fresh $La_2Ni_{0.9}V_{0.1}O_{4+\delta}$ at 550 °C.

Fig. 7. Propane conversion profile during the titration test on $La_2NiO_{4+\delta}$ at 550 °C. Carrier gas (He) flow rate, 3 ml/min; propane pulses, 10% C_3H_8 in He; sampling loop for pulsing, 300 µl.
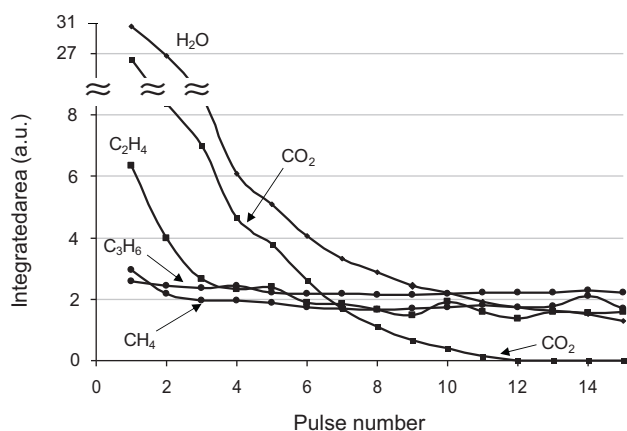
Fig. 8. Products distribution during pulse experiment at 550 °C (15 pulses) of totally re-oxidized $La_2Ni_{0.9}V_{0.1}O_{4+\delta}$.

Fig. 10. Variation of δ during pulse test on $La_2Ni_{0.9}V_{0.1}O_{4+\delta}$ at 550 °C.

which is due to consumption of oxygen in the oxide, quite similarly to results previously reported [30].

Fig. 8 shows the product distribution during pulse experiments at 550 °C of totally re-oxidized $La_2Ni_{0.9}V_{0.1}O_{4.15+\delta}$, resulting in mainly CO_2 and H_2O initially, decreasing throughout the experiment with the number of pulses, similarly the observations on fresh catalyst [30,31].

After pulse 10, CO_2 formation decreased below the MS detection threshold and the formation of C_3H_6, C_2H_4 and CH_4 remains constant. Although CO_2 is no longer produced after pulse 10, when the sample is partly reduced, it is important to stress that H_2O is formed during the whole experiment.

The scenario is different in the case of a partially re-oxidized sample with one O_2 pulse only, shown in Fig. 9. The CO_2 formation was below the MS detection threshold already for the first pulse and a constant production level of exclusively C_2H_4, CH_4 (main products) and C_3H_6 (minor product) was detected. H_2O formation continuously decreased during the experiment. It should be noted that the *y*-axis scale is different in Figs. 8 and 9.

4. Discussion

In our previous paper [30,31] we have proven that by pulsing propane, the amount of over-stoichiometric oxygen in the catalyst is depleted and, consecutively, the reactivity of the oxygen-ions decreases. At that stage, constant selectivity to olefins and inhibition of CO_2 formation is accomplished while deep oxidation
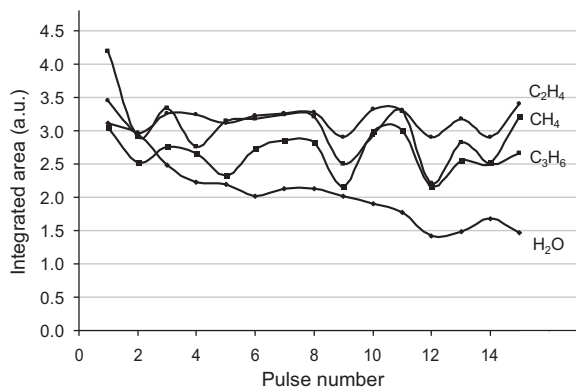

Fig. 9. Products distribution during pulse experiment (15 pulses) of partially re-oxidized $La_2Ni_{0.9}V_{0.1}O_{4+\delta}$ with one O_2 pulse at 550 °C.
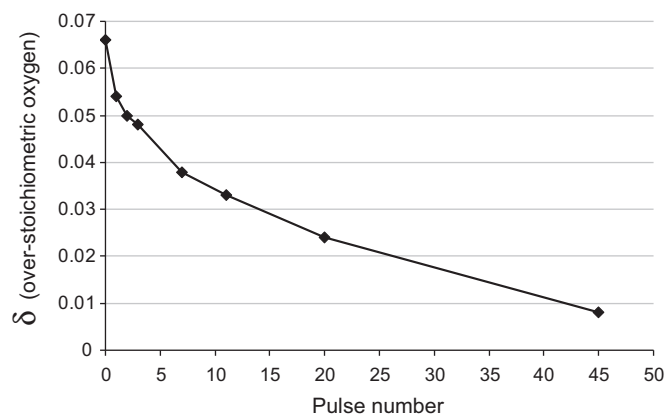
products were the main compounds at the beginning of the test, with a more oxidized sample.

In this study, the structural stability of the material when removing and re-absorbing oxygen, was investigated. Complete reversibility of removal/absorption of over-stoichiometric oxygen is demonstrated by oxidation–reduction cycles at 800 °C (Fig. 4), resulting in identical peak areas (amount of removed oxygen) and peak shapes (stability). Moreover, no structural change was observed under reducing atmosphere up to 500 °C, when all over-stoichiometric oxygen was removed (Fig. 3b). Compared to XRD on fresh material, the only difference observed was changes in the ratio of peak-intensity in the ranges between 31° and 33° as well as 42° and 48°. This is very similar to the effect of V or Cu addition to LN [30,31,37]. This is probably due to structural distortion (or stress), caused by removing over-stoichiometric oxygen. Decomposition of $La_2Ni_{0.9}V_{0.1}O_{4.15+\delta}$ catalyst in La_2O_3 and Ni^0 took place at 750 °C (Fig. 3c); such high temperature was therefore not used in the pulse experiments presented here, circumventing any phase-changes. No peaks related to V were observed, which is probably due to the low amount in the sample (1.2% by weight).

As the material showed reversibility while varying the over-stoichiometry level, the attention was focused on quantification of over-stoichiometric oxygen during pulse experiments. However, over-stoichiometry in $La_2Ni_{0.9}V_{0.1}O_{4.15+\delta}$ appears extremely sensitive to the experimental conditions. The exact pre-treatment prior to the propane pulse test, is therefore influencing the oxygen content in the catalyst and, consequently, its reactivity. As was shown with TG analysis (Fig. 5), 0.26 mmol of oxygen per gram of catalyst were removed when pretreating in He at 550 °C for 30 min. Knowing that the total amount of over-stoichiometric oxygen in the fresh sample equals to 0.41 ± 0.02 mmol/g (Fig. 4), the corresponding δ value changes from 0.170 at room temperature, to 0.066 at 550 °C. Consequently, the catalyst composition changed from $La_2Ni_{0.9}V_{0.1}O_{4.320}$ at room temperature to $La_2Ni_{0.9}V_{0.1}O_{4.216}$ at 550 °C.

Isothermal treatment at 550 °C for 14 h caused oxygen loss equal to 0.27 mmol/g, which is very similar (within 4%) to the effect of a treatment during 30 min. This is indicating relatively fast equilibration. It is evident that the catalyst also released oxygen during the pre-treatments before starting propane pulse experiments. The similarity in the numbers after 30 min and 14 h in TGA clearly show that the data can be safely used to estimate the oxygen content after pretreating in the pulse equipment. Thus, the decrease of δ during the pulse experiments at 550 °C was calculated, based on (i) the initial value of δ equal to 0.066 (Fig. 5) and (ii) the amount of removed oxygen obtained with back titration with O_2 pulses (Fig. 6). Fig. 10 shows the resulting values of δ as a function of the pulse number.
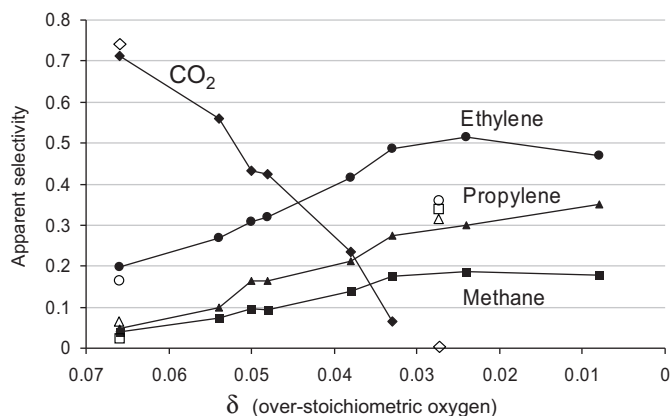
Fig. 11. Apparent selectivities of methane (■, □), ethylene (●, ○), propylene (▲, △) and CO_2 (♦, ◇) during the pulse test at 550 °C on fresh $La_2Ni_{0.9}V_{0.1}O_{4.15+\delta}$ (full symbols), and on re-oxidized $La_2Ni_{0.9}V_{0.1}O_{4.15+\delta}$ (open symbols). The two sets of open symbols represent apparent selectivity of totally ($\delta = 0.066$) and partially ($\delta = 0.028$) re-oxidized catalyst.

As expected, the value of δ decreased with the number of pulses, resulting in a δ value of 0.008 after 45 pulses. Clearly, over-stoichiometric oxygen is the active species for propane conversion throughout the whole experiment. In a separate experiment not shown here, the over-stoichiometric oxygen was completely removed via pre-treatment in He up to 550 °C and switching to C_3H_8 flow for 30 min at same temperature. Complete oxygen removal was confirmed by means of back titration with oxygen pulses in He atmosphere. The amount of removed oxygen by flowing C_3H_8 during 30 min was quantified as 0.18 mmol/g, in good agreement with the amount of residual over-stoichiometric oxygen at 550 °C in He atmosphere. This amount of over-stoichiometric oxygen remaining in the sample at 550 °C in inert atmosphere (before to switch to C_3H_8 flow) is equal to the amount of reactive oxygen available during pulse experiment at same temperature, resulting in conversion and product distribution as described in or previous work [30,31]. Subsequent propane pulses, without back titration with oxygen, resulted in zero conversion, demonstrating that the catalyst is not active when over-stoichiometric oxygen is removed completely. It is interesting to notice that the amount of oxygen removed during the pretreatment in inert from 25 to 550 °C (0.26 mmol/g, according to TGA), added to the amount of oxygen removed during the pre-treatment in C_3H_8 at 550 °C (0.18 mmol/g), is in very good agreement with the total amount of over-stoichiometric oxygen removed by H_2-TPR (0.41 ± 0.02 mmol/g) at same temperature.

In our previous papers [30,31] we have reported that the product distribution changes throughout the pulse experiment. Now, it is possible to relate the selectivity change to the variation in δ, as shown in Fig. 11 (full symbols). The two sets of open symbols in the same figure represent the apparent selectivity of completely and partially re-oxidized catalysts. Initially, the activity of oxygen is too high, resulting in mainly deep oxidation products. Decreasing the amount of over-stoichiometric oxygen, the formation CO_2 decreases and the apparent selectivity toward olefins increases. The CO_2 level is below the MS detection limit for values of δ below 0.030 (catalyst composition $La_2Ni_{0.9}V_{0.1}O_{4.18}$) resulting in maximal selectivity toward olefins.

Instead of varying δ via removing oxygen by pulsing with propane, the δ value can also be modified by partial, instead of complete, re-oxidation after pulsing propane. The open symbols in Fig. 11 present the results. First, complete re-oxidation restores the performance of the material completely, as reported earlier [30,31]. Partial oxidation, restoring δ to 0.028, results in a similar result as compared to the same δ value achieved via propane pulsing, in the

sense that in both cases CO_2 formation is below the detection limit whereas ethylene, propylene and methane are being formed. However, the ratio of these products is quite different, indicating that partial re-oxidation does not result in the same thermodynamically equilibrated material, resulting from pulsing propane. We suggest that O-concentration gradients, and thus δ gradients, result from partial re-oxidation, either along the reactor axis or within the solid oxide due to bulk diffusion. It should be noted though that during pulsing not only the product distribution changes, but also the propane conversion changes (Fig. 7); therefore we cannot rule out that consecutive reactions are involved in the change in product distribution as observed.

Anyhow, the results clearly show that good selectivity to olefins can be expected using $La_2Ni_{0.9}V_{0.1}O_{4.15+\delta}$, provided that the over-stoichiometry at the surface exposed to the alkane is maintained in the range $0.00 < \delta < 0.030$. Therefore, the reactivity of the material is suitable for operation of a dense membrane reactor, provided that the surface of the membrane exposed to propane is in equilibrium with δ values in this window. Obviously, additional hurdles, e.g. sufficient permeability and mechanical strength, must be taken before actual operation of a dense membrane reactor can be realized.

5. Conclusions

The reactivity of $La_2Ni_{0.9}V_{0.1}O_{4.15+\delta}$ with propane at 550 °C strongly depends on δ. When $\delta > 0.03$ the main product is CO_2, whereas selective conversion to propylene, ethylene and methane is achieved when $0.00 < \delta < 0.03$. Furthermore, oxidation–reduction cycles in propane and oxygen at 550 °C are reversible and the material is stable. Therefore, based on its chemical properties $La_2Ni_{0.9}V_{0.1}O_{4.15+\delta}$ is a promising option for selective oxidative dehydrogenation of propane with a dense membrane reactor, providing that the degree of over-stoichiometry is limited to 0.03 at the surface of the catalyst.

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