Role of CO2 During Oxidative Dehydrogenation of Propane Over Bulk and Activated-Carbon Supported Cerium and Vanadium Based Catalysts

Petar Djinović1,5 · Janez Zavašnik2,3 · Janvit Teržan1 · Ivan Jerman4

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Abstract
CeO2, V2O5 and CeVO4 were synthesised as bulk oxides, or deposited over activated carbon, characterized by XRD, HRTEM, CO2-TPO, C3H8-TPR, DRIFTS and Raman techniques and tested in propane oxidative dehydrogenation using CO2. Complete oxidation of propane to CO and CO2 is favoured by lattice oxygen of CeO2. The temperature programmed experiments show the ~ 4 nm AC supported CeO2 crystallites become more susceptible to reduction by propane, but less prone to re-oxidation with CO2 compared to bulk CeO2. Catalytic activity of CeVO4/AC catalysts requires a 1–2 nm amorphous CeVO4 layer. During reaction, the amorphous CeVO4 layer crystallises and several atomic layers of carbon cover the CeVO4 surface, resulting in deactivation. During reaction, V2O5 is irreversibly reduced to V2O3. The lattice oxygen in bulk V2O5 favours catalytic activity and propene selectivity. Bulk V2O3 promotes only propane cracking with no propene selectivity. In VOx/AC materials, vanadium carbide is the catalytically active phase. Propane dehydrogenation over VC proceeds via chemisorbed oxygen species originating from the dissociated CO2.

Graphic Abstract

Keywords Propene · Oxidative dehydrogenation · CO2 · Lattice oxygen · Reaction mechanism

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Petar Djinović petar.djinovic@ki.si
1 Department of Inorganic Chemistry and Technology, National Institute of Chemistry, Hajdrihova 19, 1000 Ljubljana, Slovenia
2 Jožef Stefan Institute, Jamova cesta 39, 1000 Ljubljana, Slovenia
3 Max-Planck-Institut Für Eisenforschung GmbH, Max-Planck-Straße 1, 40237 Düsseldorf, Germany
4 Department of Materials Chemistry, National Institute of Chemistry, Hajdrihova 19, 1000 Ljubljana, Slovenia
5 University of Nova Gorica, Vipavska 13, 5000 Nova Gorica, Slovenia

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1 Introduction

Propene is an important commodity chemical in the petrochemical industry and is used for the synthesis of polypropylene, propylene oxide, acrylonitrile, cumene, butyraldehyde, acrylic acid, etc. It is currently produced in the amount of ~100 Mt/year, mainly by naphtha steam cracking and FCC (fluidised catalytic cracking) technologies. In recent years, a growing gap between the demand and supply of propene is becoming apparent, which calls for the implementation of additional propene production pathways [1]. Catalytic oxidative dehydrogenation of propene using O2 or CO2 emerge as possible solutions. The propane-O2 ODH reaction is thoroughly researched and supported VOx catalysts have been the focus of many experimental [2, 3] and theoretical studies [4]. The support strongly influences the performance of these catalysts and precise active site architecture is required to promote propene dehydrogenation instead of total combustion to COx [1]. Also, propane conversion and propene selectivity are strongly inversely connected due to facile activation of sp2 hybridised C=C bond in propene, which promotes its further oxidation.

The propane-CO2 ODH reaction (reaction 1) has some benefits, as well as drawbacks. It reduces CO2 to CO and could be implemented for CO2 valorisation and reduction of anthropogenic CO2 emissions.

\[
C_3H_8 + CO_2 \leftrightarrow C_3H_6 + CO + H_2O \quad \Delta H_{298K} = 167 \text{kJ/mol} \tag{1}
\]

The reaction is endothermic, thermodynamically restricted, and favours carbon formation in a broad range of reaction conditions [5]. Thermodynamic analysis has shown that surplus CO2 in the feed has the potential to alleviate the reaction conditions [5]. Thermodynamic analysis has shown restricted, and favours carbon formation in a broad range of alkene oxidation [10, 11].

Several metal oxides (bulk and supported Ga2O3, Cr2O3, and Fe2O3) were tested by Michorczyk and Ogonowski [12] in the propane-CO2 ODH reaction. Ga2O3 was identified as the most effective, with propene yield equal to 30% at 600 °C.

Zou et al. [13] investigated the effect of chromium loading in CrOx/SiO2 catalysts and established the following decreasing order of propane conversion and propene selectivity: 2.5 wt% CrOx/SiO2 > 5 wt% CrOx/SiO2 > 10 wt% CrOx/SiO2. UV–Vis spectroscopic analysis indicated that ODH activity correlates with highly dispersed chromates, such as Cr6+ ions in the form of mono, di and polychromates. With increasing chromium loading above 3 wt%, the presence of bulk Cr2O3 was identified. Deactivation of the catalyst with time on stream was observed and related to coke accumulation and changes in chromate speciation from oligomeric to bulk crystalline Cr2O3.

Martinez Huerta et al. [14] studied catalysts containing 2 and 5 wt. % vanadium dispersed over CeO2 for ethane-O2 ODH reaction. The operando Raman-GC analysis showed stepwise dispersion of V2O5 into surface VOx, before the formation of the amorphous CeVO4 phase. In the CeVO4 phase, vanadium maintains its 5+ oxidation state and redox activity is related only to Ce4+ ↔ Ce3+. The initially formed amorphous CeVO4 converts into a well crystalline CeVO4 phase as the reaction temperature increases. These authors also suggest that the V–O–Ce bond must be the active phase. Increased crystallinity decreases the number of exposed V–O–Ce bonds due to the lower surface-to-volume ratio, which accounts for catalyst deactivation.

Ascoop et al. [15] studied a WOx–VOx/SiO2 catalyst and using isotopic labelling confirmed that in parallel to an oxidative dehydrogenation pathway (reaction 1), also reverse water gas shift reaction (H2 + CO2 ↔ CO + H2O) and a direct, non-oxidative propane dehydrogenation reactions (C3H8 ↔ C3H6 + H2) occur over the catalyst at 600 °C. According to their DFT calculations, C-H bond activation in propane is the rate-limiting reaction step, whereas catalyst re-oxidation (V3+ to V4+) with CO2 occurs much faster.

Turakulova et al. [16] observed that the interaction between supported VOx and Ce0.46Zr0.54O2 results in the formation of CeVO4, which is the active phase responsible for propane ODH. The full oxidation of propane to COx is reported to be catalysed at the CeZrO2 surface, whereas propene is formed over CeVO4. The oxygen exchange properties of the catalyst play an essential role in the ODH reaction. Contrary to Ascoop et al. [15], Turakulova et al. report that re-oxidation of the active sites is the rate-limiting step of the process, which is associated with the redox properties of the VOx/Ce0.46Zr0.54O2 catalyst.

Nowicka et al. [17] studied propane-CO2 ODH reaction over Pd/CeZrAlOx catalysts and showed that over ceria-based catalysts, the reaction proceeds via the Mars van
Krevelen mechanism in parallel with the RWGS reaction. The high propene selectivity (95% at ~3% propane conversion) was attributed to the exclusive formation of selective oxide (O²⁻) ions when CO₂ dissociates at the surface oxygen vacancy sites of CeO₂. The role of Pd is to enhance the reducibility and to accelerate the re-oxidation of the CeO₂−x surface. Strong catalyst deactivation was attributed to carbon accumulation which blocks the active sites and incomplete catalyst oxidation by CO₂.

Carbon materials with a high surface area and large pore volume have an increasing number of applications as catalyst supports and adsorbents [18–20]. They can be synthesized in a variety of morphologies (nanotubes, ordered mesoporous structures, etc.) and their surfaces can be functionalized with adatoms (V and N) or oxygen containing groups, giving rise to catalytic activity in many reactions, including oxidative dehydrogenation of propane [21–23].

Our common observation in many propane-CO₂ ODH studies is that catalytic tests were run at relatively high reaction temperatures (600–700 °C) in order to activate CO₂ and ensure reasonable conversions. Under such conditions, thermal (noncatalytic) reactions strongly contribute to the observed propane conversion and influence the distribution of reaction products [7, 15].

This work is focused on the systematic analysis of propane-CO₂ interaction with bulk and activated carbon (AC) supported VOₓ, CeO₂ and CeVO₄ catalysts. Vanadia based materials are very often investigated catalysts in the oxidative dehydrogenation of parafines [1], whereas ceria is known for its reactivity towards CO₂ [24]. Consequently, these materials, as well as their mixed oxide phase (CeVO₄) were the subject of this investigation. Structural, redox, and chemical nature of the active phases were varied by changing their loading on the AC support and were correlated to activity, stability, and olefin selectivity in the propane-CO₂ ODH reaction.

2 Experimental

2.1 Synthesis of Catalysts

Bulk V₂O₅ was synthesised by calcination of vanadium acetyl-acetonate (Sigma Aldrich, purity 99%). Bulk CeVO₄ was synthesised by completely dissolving 92 mg of NH₄VO₃ (Sigma Aldrich, p.a.) in 65 ml of ultrapure water (resistivity of 18.2 MΩ, Elga Purelab Option-Q), while the solution was heated to 80 °C and stirred with a magnetic stirrer. To prevent water evaporation, the glass beaker was covered with a petri dish. Once dissolved, 1 drop of concentrated HNO₃ was added. In a separate glass beaker, 340 mg of Ce(NO₃)₃ × 6H₂O (Sigma Aldrich, purity 99%) was dissolved in 10 ml of ultrapure water. After complete dissolution, the prepared solutions were mixed, resulting in an instantaneous formation of a yellow–brown precipitate. The suspension was stirred at 80 °C for an additional 2 h. After cooling, filtering and washing 3 times with ultrapure water, the suspension was dried overnight at 70 °C in a laboratory drier. Pure CeO₂ was synthesised by dissolving 4.9 g of Ce(NO₃)₃ × 6H₂O (Sigma Aldrich, purity 99%) in 84 ml of ultrapure water. This solution was mixed with 140 ml of 0.1 M aqueous NaOH and stirred for 30 min. Afterwards, it was transferred to Teflon® lined autoclaves (~35 ml volume), which were placed into a laboratory drier preheated to 180 °C and kept at this temperature for 24 h. The precipitate was filtered, washed 3 times with ultrapure water, and dried overnight at 70 °C in a laboratory drier. All bulk catalysts were calcined 4 h at 600 °C (Nabertherm, model LT 9/11, heating ramp of 2 °C/min) in static air.

Synthesis of catalysts containing CeVO₄ (10–40 wt% CeVO₄) supported on activated carbon (AC) was similar to the one of bulk CeVO₄ with the following exceptions: 0.7 g of activated carbon, finely ground in an agate mortar, was added to the aqueous NH₄VO₃ solution. After filtration the samples were dried overnight at 70 °C. The VOₓ (2–12 wt% vanadium) was deposited over AC by dissolving appropriate amounts of NH₄VO₃ in 10 ml of ultrapure water at 80 °C. Afterwards, 0.7 g of AC was added, stirred for another 2 h at room temperature, filtered and dried overnight at 70 °C in a laboratory drier. CeO₂ (7–17 wt% cerium) was deposited over AC by dissolving appropriate amounts of Ce(NO₃)₃ × 6H₂O in 1 ml ultrapure water. Afterwards, 0.7 g of AC was added, mixed for 2 h and dried overnight at 70 °C. All AC supported catalysts were calcined (4 h at 600 °C, 2 °C/min heating ramp) in a tubular oven (Carbolite, model HST 12/400) in Argon (20 l/h) to prevent AC oxidation. The CeVO₄ content in the CeVO₄/AC catalysts was selected so the actual content of vanadium or cerium in the CeVO₄ phase covered a similar range as in CeO₂/AC or VOₓ/AC catalysts. Actual content of vanadium, cerium and CeVO₄ is shown in Table S1.

2.2 Characterisation and Catalytic Testing

XRD analyses were performed on a PANalytical X’pert PRO diffractometer using Cu Kα radiation (λ= 0.15406 nm) between 2theta angles of 10° and 80° with the step size of 0.034°. The BET specific surface area, total pore volume and average pore size were determined using N₂ adsorption/desorption isotherms at 77 K (Micromeritics, model TriStar II 3020). The samples were degassed before measurements using a SmartPrep degasser (Micromeritics) in a N₂ stream 1 h at 90 °C followed by 4 h at 180 °C. Actual vanadium, cerium and CeVO₄ contents were determined from the mass of oxidic residue remaining after complete oxidation of the AC support (TGA apparatus, model STA6000 by Perkin
Elmer) by heating the samples in air (25 ml/min) with a heating ramp of 10 °C/min to 800 °C. The carbon content, accumulated on the bulk catalyst during reaction was analysed by CHNS analytical technique (Series II CHNS analyser, model 2400 from Perkin Elmer).

Prior to TEM analysis, samples were dispersed in absolute ethanol and sonicated for 30 s, then directly transferred to Cu lacey carbon support grids. As prepared samples were analysed by 200 kV transmission electron microscope (TEM, JEM-2010F, Jeol Inc.) and by C$_e$-corrected (TEM, Titan Themis G$^3$, FEI Inc., equipped with CEOS CETCOR aberration corrector) operating at 300 kV. Amount of carbon deposited on the bulk unsupported catalysts during the catalytic reaction was analysed using CHNS elemental analyser (Perkin Elmer, model 2400).

Catalyst reduction with propane (C$_3$H$_8$-TPR) and oxidation with CO$_2$ (CO$_2$-TPO) was analysed in the Micromeritics Autochem 2920 apparatus. The powdered samples (100 mg) were positioned on a flock of quartz wool inside a U-shaped quartz reactor. The samples were pre-treated with He (Linde, purity 5.0) for 30 min at 300 °C, followed by cooling to 10 °C, switching to a 50% C$_3$H$_8$/He flow (10 ml/min) and heating to 600 °C with a 10 °C/min ramp. The samples were again cooled to 10 °C, and re-oxidation by CO$_2$ (Linde, purity 5.3) was started by increasing the temperature until 700 °C with a 10 °C/min ramp. The analytical protocol is shown in Fig. S1. Reaction products were monitored by mass spectrometry (model Thermostar®, Pfeiffer Vacuum) propane (m/z = 29), propene (m/z = 41), ethene and ethane (m/z = 27), methane (m/z = 15), water (m/z = 18), CO$_2$ (m/z = 44), He (m/z = 4) and H$_2$ (m/z = 2).

Transient interaction of bulk CeVO$_4$, CeO$_2$, and V$_2$O$_5$ with propane and CO$_2$ was analysed with Diffuse Reflectance Infrared Furrer Transformed Spectroscopy (DRIFTS) analysis (Perkin Elmer, model Frontier) equipped with DiffusIR cell from Pike Scientific. Approximately 10 mg of finely powdered sample was pre-treated in 20%O$_2$/He stream at 550 °C for 15 min. Afterwards, the sample was exposed to the following sequence of atmospheres: 20% O$_2$/He → 20% C$_3$H$_8$/He → 20% CO$_2$/He. Sample spectra were recorded continuously (4 s between scans) in the range between 500 and 4000 cm$^{-1}$, 8 accumulations per scan and spectral resolution of 4 cm$^{-1}$.

Raman analysis of the powdered catalysts was performed in the spectral range from 70 to 3700 cm$^{-1}$ using Witec Alpha 300 spectrometer that employed green laser with excitation wavelength of 532 nm and resolution of 4 cm$^{-1}$ at 30 mW laser power.

Catalytic experiments were performed in a PID Eng&Tech reactor system using a quartz tubular reactor (10 mm I.D.). The powdered catalyst (300 mg) was positioned between two flocks of quartz wool. Reaction temperature was measured with a K-type thermocouple, which was covered by a quartz sleeve, thus minimising the heated volume inside the reactor above the catalyst bed. A quartz rod was used to minimise the reactor volume after the catalyst bed. This reduced the occurrence of thermal, non-catalytic reactions (verified with a blank experiment which showed <0.5% propane conversion at 550 °C. Before the catalytic reaction, the catalyst was heated using a heating ramp of 10 °C/min in a flow of CO$_2$ (Linde, purity 5.3) and He (Linde, purity 5.0) with a flowrate of 10 ml/min each, until reaching the reaction temperature of 550 °C. Afterwards, the propane flow (Linde, purity 3.5, 10 ml/min) was added and 15 min were allowed before starting the GC analysis to allow for stabilization of gas concentrations. Agilent 7890A gas chromatograph (equipped with Molesieve 5A and Poraplot Q columns and two TCD detectors) was used for qualitative and quantitative analysis of gas stream. The carbon mass balances were in all cases between 85 and 104%. Operation in kinetic regime was ensured by plotting the propane reaction rate versus progressively increasing C$_3$H$_8$/CO$_2$/He flowrate over a constant mass of catalyst (Fig. S2). Details on calculation of propane conversion and product selectivities are provided in the Supplementary information.

## 3 Results

### 3.1 Catalytic Activity of Bulk CeO$_2$, V$_2$O$_5$ and CeVO$_4$

Catalytic performance of all materials during propane-CO$_2$ ODH reaction is summarized in Tables 1 and 2.

Main reaction product over bulk CeO$_2$ was CO, along with CH$_4$ and H$_2$ (71, 10 and 13% selectivity, respectively). The olefin selectivity was low (12% for propene and 4% for ethene).

The bulk V$_2$O$_5$ deactivated quickly: the initial propane conversion of 9.5% stabilised at 3.2% after 240 min TOS (Fig. 1a). Also, C$_3$H$_6$ selectivity decreased from 27 to 0% (Table 1 and Fig. 1b) and CO dropped to zero in 140 min (not shown). Contrary, selectivities for H$_2$ and CH$_4$ increased slowly during the experiment from 9 to 25% and 31 to 61%, respectively. This transient behaviour of the V$_2$O$_5$ catalyst indicates drastic changes in contribution of several possible reaction pathways occurring during propane-CO$_2$ ODH reaction: (i) oxidative dehydrogenation with participation of lattice oxygen producing propene and water, (ii) oxidative dehydrogenation with CO$_2$ acting as the oxidant, producing propene, CO and water (iii) total oxidation of propane to CO and water, (iv) nonoxidative dehydrogenation pathway producing propene and hydrogen and (v) propane cracking to CH$_4$, H$_2$ and carbon which deposits over the catalyst’s surface (reactions 1–4). The relevance of these reactions will be discussed in detail in the following sections.
Activity of bulk CeVO₄ was stable, as well as selectivity for all reaction products: C₃H₆, CH₄, H₂ and C₂H₄ at 25, 31, 26 and 18%, respectively. No CO was formed, which indicates the lattice oxygen or CO₂ participation (Reaction 1) and RWGS reaction (CO₂ + H₂ → H₂O + CO) are not occurring over this catalyst. The non-oxidative dehydrogenation and propane/propane cracking dominate the reaction product distribution over bulk CeVO₄. Results of a blank experiment (Fig. S3) show that no conversion is taking place at 550 °C in the empty reactor. This confirms the non-oxidative dehydrogenation reaction is a consequence CeVO₄.

### 3.2 Catalytic Activity of AC Supported Catalysts

#### 3.2.1 CeO₂/AC Catalysts

Propane conversions and propene selectivities were notably higher over CeO₂/AC catalysts compared to bulk CeO₂ (Table 1). A notable (~50%) decrease in propane conversion in the initial 60 min of reaction for 7CeO₂/AC (Fig. 2a) was accompanied by an increase in propene selectivity.

#### 3.2.2 VOₓ/AC Catalysts

Catalytic stability of VOₓ/AC catalysts is notably improved compared to bulk V₂O₅ (Table 1, Figs. 1A and 2A). Propene selectivities ranged between 40 and 51% and were marginally influenced by vanadium content, which was varied between 2 to 12 wt%. Selectivities for CO were between 41 and 50%, for H₂ ranged between 8 and 10%, for CH₄ between 5–6% and for C₂H₄ between 1–2% (Table 2). Contrary to the complete loss of propene selectivity over bulk V₂O₅, the propene selectivity over VOₓ/AC catalysts was stable during the 240 min of reaction (Fig. 2b). This indicates markedly different catalytic behaviour of supported vanadium species compared to bulk V₂O₅.

**Table 1** Initial propane conversion, propane reaction rate, propene selectivity and propene yield at 550 °C. Numbers in parentheses represent values after 240 min of reaction

| Catalyst sample | C₃H₈ conversion (%) | Propane reaction rate, μmol/gcat min | C₃H₆ selectivity (%) | C₃H₆ yield (%) |
|-----------------|---------------------|--------------------------------------|---------------------|----------------|
| AC              | 2 (2)               | 30                                   | 28 (19)             | 0.6 (0.4)      |
| CeO₂            | 5.6 (4.1)           | 84                                   | 10 (12)             | 0.6 (0.5)      |
| V₂O₃            | 9.4 (3.2)           | 141                                  | 27 (0)              | 2.5 (0)        |
| CeVO₄           | 4.3 (3.6)           | 65                                   | 28 (26)             | 1.2 (0.9)      |
| 2VOₓ/AC         | 12.3 (5.8)          | 185                                  | 28 (40)             | 3.4 (2.3)      |
| 5VOₓ/AC         | 10.5 (6.2)          | 155                                  | 37 (51)             | 3.9 (3.2)      |
| 12VOₓ/AC        | 13.8 (7.7)          | 207                                  | 36 (44)             | 4.9 (3.4)      |
| 7CeO₂/AC        | 12.4 (4.8)          | 184                                  | 17 (34)             | 2.1 (1.6)      |
| 12CeO₂/AC       | 9.7 (3)             | 145                                  | 27 (62)             | 2.6 (1.9)      |
| 17CeO₂/AC       | 10.1 (6.4)          | 152                                  | 23 (28)             | 2.3 (1.8)      |
| 10 CeVO₄/AC     | 7 (6)               | 105                                  | 41 (29)             | 2.9 (1.7)      |
| 15 CeVO₄/AC     | 9.3 (7)             | 140                                  | 42 (43)             | 3.9 (3)        |
| 20 CeVO₄/AC     | 11.2 (8.5)          | 166                                  | 49 (57)             | 5.5 (4.8)      |
| 30 CeVO₄/AC     | 15.3 (10.1)         | 230                                  | 42 (49)             | 6.4 (4.9)      |
| 40 CeVO₄/AC     | 12.9 (7)            | 194                                  | 47 (62)             | 6.1 (4.3)      |

**Table 2** Product selectivity of AC supported catalysts after 240 min of reaction. See Supplementary Information file for details on calculation of these values

| Sample     | Selectivity (%) | C₃H₆ | C₂H₄ | CH₄ | CO | H₂ |
|------------|-----------------|------|------|-----|----|----|
| 2VOₓ/AC    | 40              | 1    | 6    | 50  | 10 |    |
| 5VOₓ/AC    | 51              | 2    | 6    | 43  | 10 |    |
| 12VOₓ/AC   | 44              | 1    | 5    | 41  | 8  |    |
| 10CeVO₄/AC | 29              | 0    | 5    | 59  | 18 |    |
| 15CeVO₄/AC | 43              | 1    | 5    | 37  | 9  |    |
| 20CeVO₄/AC | 57              | 4    | 11   | 22  | 9  |    |
| 30CeVO₄/AC | 49              | 1    | 4    | 35  | 11 |    |
| 40CeVO₄/AC | 62              | 0    | 5    | 28  | 7  |    |
| 7CeO₂/AC   | 34              | 2    | 11   | 50  | 8  |    |
| 12CeO₂/AC  | 62              | 3    | 19   | 14  | 13 |    |
| 17CeO₂/AC  | 28              | 2    | 9    | 56  | 6  |    |

C₃H₈ → C₂H₄ + CH₄

C₃H₈ → C₃H₆ + H₂

C₂H₄ → CH₄ + C


3.2.3 CeVO₄/AC Catalysts

Testing of CeVO₄/AC catalysts revealed a positive correlation between CeVO₄ content and catalytic activity, as well as propene selectivity. The 30CeVO₄/AC sample achieved 11.4% propane conversion and 57% propene selectivity at 60 min TOS (Table 1 and Fig. 2). This is clearly superior compared to all tested bulk and supported VOₓ, CeO₂ and CeVO₄ materials. For all CeVO₄/AC catalysts, a slow continuous deactivation was observed with time on stream. Selectivities for CO ranged between 22 and 59%, H₂ ranged between 8 and 18%, for CH₄ between 5 and 11% and for C₂H₄ up to 4% (Table 2).

Catalytic propane dehydrogenation reaction often suffers from poor stability, which is usually caused by carbon build-up on the catalyst, which blocks the active sites \[6\]. A long-term catalytic test was performed on the 20CeVO₄/AC catalyst (Fig. 3). Continuous deactivation was observed in the first 30 h of reaction; the catalyst lost 71% of its initial activity (based on the drop of propane conversion). Catalyst deactivation was accompanied by a slow rise in propene, CH₄, C₂H₄ and H₂ selectivities (Fig. 3), as well as decrease of CO selectivity (not shown). This indicates a slow transition from an oxidative propane-CO₂ to a non-oxidative propane dehydrogenation pathway. Finally, conversions of propane and CO₂ stabilised at 3% each. Very similar behaviour was observed over Pd/CeZrAlOₓ catalysts during propane-CO₂ ODH reaction at 600 °C by Nowicka et al.\[17\]

An important aspect for discussion of catalytic performance of AC supported catalysts is experimental verification.
that support gasification does not contribute to measured reaction products. Under simulated reaction conditions (4 h at 550 °C in a 30 ml/min total flow consisting of 33% C3H8, 33% CO2 and 33% He) inside a thermogravimetric apparatus, the mass of 20CeVO4/AC catalyst increased by 0.58 wt. % (Fig. S4A). This experiment confirmed a small amount of carbon was deposited on the catalyst during the 4 h of reaction. Additionally, the TGA-TPO experiment of fresh and spent 20CeVO4/AC catalysts after 45 h of reaction showed the weight fraction of carbon in the sample increased by 0.62 wt% (Fig. S4B). These two experiments revealed no gasification of the AC support during catalytic reaction and that carbon accumulation on the catalyst is low and occurs mainly in the initial 4 h of reaction. Spent bulk catalysts after 4 h of propane-CO2 ODH reaction contain 1.6, 1.4 and 1.4 wt% of carbon for CeVO4, V2O5 and CeO2, respectively.

Propene selectivity at comparable propane conversions is shown in Fig. S5 for all catalysts, which revealed increasing selectivity in the following order: CeVO4 > V2O5 > CeO2.

### 3.3 Catalyst Characterisation

#### 3.3.1 N2 Physisorption and XRD Analysis

Morphological properties analysed by N2 physisorption technique are compiled in Table 2. The V2O5 and CeVO4 are mesoporous with total low pore volumes and BET specific surfaces, whereas specific surface area of CeO2 is much higher. After 4 h of reaction, the specific surface area of CeO2 drops by about 50%, whereas changes for V2O5 and CeVO4 were much smaller. The specific surface area and pore volume of supported catalysts are dominated by the microporous activated carbon support. With increasing content of the active phase (VOx, CeO2 or CeVO4), a continuous decrease of specific surface area and pore volume are observed, which is in line with a progressively larger contribution from the deposited oxides.

XRD analysis was performed on the fresh and spent catalysts (Figs. 4, 5 and S6). In bulk CeVO4 and CeVO4/AC samples (Fig. 4a), only a CeVO4 phase (PDF 00-012-0757) was identified. No diffraction lines of crystalline CeO2, V2O5 or V2O3 could be identified. The Scherrer equation was applied and the average scattering domain size of the CeVO4 crystallites was calculated based on its most intense diffraction line

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**Fig. 3** Catalytic performance of 20CeVO4/AC catalyst during the propane-CO2 ODH stability test. Please refer to online version of this manuscript for colour figure

**Fig. 4** a XRD patterns of fresh bulk CeVO4 and CeVO4/AC catalysts and b V2O5 before and after 4 h of propane-CO2 ODH reaction. Please refer to online version of this manuscript for colour figure
at 2θ = 24°. For bulk CeVO$_4$, the calculated average scattering domain size was 80 nm, whereas for the AC supported CeVO$_4$ catalysts this value was lower and increased from 25 nm in the 10CeVO$_4$/AC to 33 nm in the 40CeVO$_4$/AC sample. These results indicate the AC supports limits the crystal growth of the CeVO$_4$. The XRD results of 20CeVO$_4$/AC sample before, and after 4 and 45 h of propane-CO$_2$ ODH reaction (Fig. S6) showed no structural changes in the CeVO$_4$ and negligible sintering since the average crystallite size measured 24, 25 and 26 nm, respectively. The average pore diameter of AC supported catalysts is below 2 nm, which indicates that CeVO$_4$ crystallites observed by XRD, which are more than an order of magnitude larger, reside in the interparticle voids of the AC support.

XRD analysis of bulk V$_2$O$_5$ sample before and after propane-CO$_2$ ODH reaction (Fig. 4b) shows that the initially present V$_2$O$_5$ phase (PDF 01-089-0612), is reduced and quantitatively transformed to V$_2$O$_3$ (PDF 01-071-0342). Results for the VO$_x$/AC samples before and after catalytic tests are shown in Fig. 5a. The broad reflection peaks between 20°–30° and 40°–50° are visible on all samples and originate from activated carbon. The diffraction lines at 21.8°, 26.6° and 35.8° can be ascribed to SiO$_2$ cristobalite*, quartz# and graphite$ (PDF 01-089-3435, 01-085-1780 and 01-075-2078, respectively). These crystalline phases are present in the pristine activated carbon. The amount of SiO$_2$ in the AC was determined to be 1.1 wt% (thermogravimetric heating of pristine AC sample in air, followed by SEM-EDXS analysis of inorganic, non-combustible residue). No diffraction peaks from vanadium containing crystalline phases could be identified in the 2VO$_x$/AC and 5VO$_x$/AC samples.

In the fresh 12VO$_x$/AC sample weak diffraction lines at characteristic positions for V$_2$O$_3$ became apparent (PDF 01-071-0342). Formation of V$_2$O$_3$ is triggered by sample calcination in argon (see experimental section). The intensity of diffraction lines belonging to V$_2$O$_3$ increased after 4 h of reaction, revealing its sintering.

Figure 5b shows XRD results of bulk and supported CeO$_2$/AC catalysts. In all samples, only diffraction lines belonging to CeO$_2$ (PDF 00-034-0394) were identified. Average crystallite size in bulk CeO$_2$ was 15 nm (calculated by the Scherrer equation).

Broad diffraction lines characteristic of CeO$_2$ were identified in the CeO$_2$/AC catalysts with the average crystallite size of 4 nm which did not change with increasing CeO$_2$ content from 7 to 17 wt%. Negligible growth of CeO$_2$ crystallites occurred during the catalytic reaction, as average crystallite size of CeO$_2$ after reaction increased to 5 nm (Table 3). The AC support efficiently prevented sintering of the deposited CeO$_2$ during the reaction.

3.3.2 TEM Analysis

To explore the rapid drop of the catalytic performance, the 20CeVO$_4$/AC sample was analysed before and after 45 h of reaction (Fig. 6). In the fresh sample, the individual CeVO$_4$ crystals are agglomerated in larger clusters, deposited on the outer surface of AC support. The average CeVO$_4$ particle size measured 24 nm (Fig. S7A), which is in line with XRD estimation (Table 2). Selective area electron diffraction (SAED) pattern analysis confirmed the presence of a crystalline CeVO$_4$ phase only (Fig. 6, inset). The CeVO$_4$ crystallites have a plate-like polyhedral shape.

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Fig. 5  a XRD patterns of VO$_x$/AC and b CeO$_2$/AC catalysts before and after 4 h propane-CO$_2$ ODH tests. Please refer to online version of this manuscript for colour figure.
and well developed 3D morphology (bulges and cavities) and are additionally covered with a thin (1–2 nm) amorphous layer of CeVO₄.

After the 45 h catalytic test, negligible increase in CeVO₄ crystallite size could be measured (Fig. S7B), which is in line with the XRD analysis. However, two changes were observed on the large majority of visualized CeVO₄ crystallites: (i) the amorphous layer present in the fresh sample was absent and (ii) CeVO₄ crystallites were covered with 2–3 atomic layers of amorphous carbon, encapsulating the surface of the CeVO₄ NPs. More details on the characterization of the amorphous CeVO₄ layer and carbon layers are provided in the supplementary information and Figs. S8–S10.

In order to visualize and analyse the catalytically active phase in the 5VOₓ/AC catalyst, TEM-SAED analyses were performed (Fig. 7). It was observed that the activated carbon was covered by cubic crystallites measuring 3–10 nm in size. Selective area electron diffraction (SAED) pattern analysis identified these crystals as a cubic vanadium carbide phase (Fig. 7d). No vanadium oxides (crystalline V₂O₅ or V₂O₃) could be identified.

### Table 3

| Sample     | BET (m²/g) | Total pore volume (cm³/g) | Average pore diameter (nm) | Crystallite site² (nm) |
|------------|------------|---------------------------|---------------------------|------------------------|
| V₂O₅       | 10 (9)     | 0.05 (0.04)               | 19.2 (20.2)               | 101                    |
| CeO₂       | 74 (39)    | 0.15 (0.08)               | 7.8 (8)                   | 15                     |
| CeVO₄      | 5 (5)      | 0.01 (0.01)               | 10.4 (9.7)                | 80                     |
| AC         | 1455       | 0.71                      | < 2                       | –                      |
| 10CeVO₄/AC | 1446       | 0.76                      | < 2                       | 25                     |
| 15CeVO₄/AC | 1133       | 0.60                      | < 2                       | 26                     |
| 20CeVO₄/AC | 1138 (1105)| 0.62 (0.54)               | < 2                       | 24 (25)                |
| 30CeVO₄/AC | 1026       | 0.54                      | < 2                       | 32                     |
| 40CeVO₄/AC | 826        | 0.45                      | < 2                       | 33                     |
| 2VO₅/AC    | 1462       | 0.74                      | < 2                       | NA                     |
| 5VO₅/AC    | 1254       | 0.66                      | < 2                       | NA                     |
| 12VO₅/AC   | 1007       | 0.53                      | < 2                       | NA (22)                |
| 7CeO₂/AC   | 1236       | 0.64                      | < 2                       | 4 (5)                  |
| 12CeO₂/AC  | 1138       | 0.59                      | < 2                       | 4                     |
| 17CeO₂/AC  | 1066       | 0.55                      | < 2                       | 4 (5)                  |

Values in parentheses indicate values obtained for catalysts after the 4 h of propane-CO₂ ODH catalytic test.

²Calculated from XRD data. NA: No diffraction lines of vanadium containing phases are distinguishable in the catalysts.

### 3.3.3 Temperature Programmed Reduction with Propane (C₃H₈-TPR)

Catalyst interaction with propane (Fig. 8) and CO₂ (Fig. 9) was tested according to the protocol shown in Fig. S1. These experiments investigated: (a) the ability of lattice oxygen to react with propane, (b) the re-oxidation of the reduced catalyst by CO₂, and how these processes are influenced by the morphology of the VC, VOₓ, CeO₂ and CeVO₄ phases. During the C₃H₈-TPR experiments, CO₂ and water were identified in parallel to propane conversion (drop of propane signal in Fig. 8), indicating participation of lattice oxygen in the propane conversion.

Propane signal as a function of temperature over CeO₂ containing catalysts is shown in Fig. 8a. Several broad, low-intensity bands are apparent between 150 and 500 °C in CeO₂/AC samples, which is absent in bulk CeO₂. These are likely related to propane reacting with coordinatively unsaturated surface lattice oxygen, which are more reactive in 4 nm CeO₂ crystallites (present in all CeO₂/AC samples), compared to bulk CeO₂ (15 nm). Propane conversion lights-off between 495 and 508 °C for AC supported samples, whereas a higher temperature (530 °C) is required for propane activation over bulk CeO₂.

Bulk CeVO₄ shows negligible activity for reduction by propane up to 600 °C (black line in Fig. 8b). However, propane is able to reduce the CeVO₄/AC samples already between 480 and 505 °C, producing propene and water.

Over bulk V₂O₅, propane is oxidized extensively in the low temperature region between 350 and 500 °C producing propene and water. These results are consistent with the oxidative dehydrogenation pathway involving lattice oxygen and reduction of V₂O₅ to V₂O₃. The second propane consumption signal between 500 and 600 °C produces methane and especially hydrogen. This is consistent with catalytic tests at TOS > 140 min (Fig. 1). Propane cracking inevitably produces carbon deposition, but this could not be analysed.

The VOₓ/AC catalysts containing either only VC (2VOₓ/AC and 5VOₓ/AC) or a combination of VC and V₂O₅ (12VOₓ/AC) are starting to decompose propane at about 485 °C. In all cases, propane conversion produces propene and hydrogen (Fig. 8c).

In all analysed samples, higher propane conversion during C₃H₈-TPR experiments (Fig. 8) generally correlates with higher catalytic activity (Table 1).

### 3.3.4 Temperature Programmed Oxidation with CO₂ (CO₂-TPO)

In situ oxidation experiments with CO₂ were performed on the catalysts previously exposed to the C₃H₈-TPR protocol (Fig. S1). During CO₂-TPO, CO₂ is dissociated over the catalyst to CO and O. The latter oxidizes the catalyst and
Fig. 6 TEM micrographs of 20 CeVO₄/AC catalyst before (upper row) and after (lower row) 45 h propane-CO₂ ODH test. SAED simulation (inset) was calculated using crystal structure data for tetragonal CeVO₄ (SG141, I41/amd) [25]

Fig. 7 TEM micrographs of fresh 5VOₓ/AC catalyst at different magnifications (a–c); comparison of experimental and simulated SAED for cubic VC (d)
CO desorbs. CO desorption profiles over different catalysts are shown in Fig. 9.

The re-oxidation of bulk CeO$_2$ by CO$_2$ took place with appearance of two intense CO peaks centred at 460 and 620 °C (Fig. 9a). On the other hand, the re-oxidation of CeO$_{2-x}$/AC samples was initiated at between 400 and 450 °C with a slow, continuous rise of the CO signal until the final temperature of 700 °C was reached. This reveals very different dynamics of CeO$_2$ oxidation which is strongly related to the size of CeO$_2$ crystallites.

Bulk CeVO$_4$ does not react with CO$_2$ up to 700 °C (Fig. 9b), which is in line with inertness of this sample during C$_3$H$_8$-TPR and catalytic experiment showing no CO among reaction products. Over CeVO$_4$/AC catalysts, CO starts to appear at 500 °C and its amount continuously increases with increasing CeVO$_4$ loading.
Oxidation of bulk \( \text{V}_2\text{O}_3 \) (\( \text{V}_2\text{O}_5 \) catalyst after \( \text{C}_3\text{H}_8\)-TPR) and \( \text{VO}_x/\text{AC} \) catalysts with \( \text{CO}_2 \) was initiated at 570 °C (Fig. 9c), which reveals that at the reaction temperature of 550 °C, \( \text{V}_2\text{O}_3 \) cannot be re-oxidized with \( \text{CO}_2 \). This is in line with results of Ascoop et al. [15] who report that oxidation of \( \text{WO}_x-\text{VO}_x/\text{SiO}_2 \) catalysts with \( \text{CO}_2 \) at 600 °C can only transform \( \text{V}^{3+} \) to \( \text{V}^{4+} \). Also, the VC phase is inert towards \( \text{CO}_2 \) at 550 °C.

The \( \text{C}_3\text{H}_8\)-TPR and \( \text{CO}_2\)-TPO results revealed that the reduction and re-oxidation of \( \text{CeO}_2 \), and \( \text{CeVO}_4 \) phases are strongly dependent on their morphology. Smaller \( \text{CeO}_2 \) crystals (4 nm) in \( \text{CeO}_2/\text{AC} \) are more readily reduced by propane compared to bulk \( \text{CeO}_2 \) (15 nm), whereas during re-oxidation by \( \text{CO}_2 \), the situation is reversed. Both processes are possible at 550 °C, which was also the temperature during propane-CO2 ODH reaction.

The \( \text{CeVO}_4/\text{AC} \) samples can be reduced by propane and oxidized by \( \text{CO}_2 \) at 550 °C. This ability is absent in bulk \( \text{CeVO}_4 \), which has negligible activity for propane and \( \text{CO}_2 \) activation.

In the case of \( \text{VO}_x/\text{AC} \) catalysts, the vanadium containing phase depends on the vanadium content (\( \text{V}_2\text{O}_3 \) in bulk sample, \( \text{VC} \) in \( 2\text{VO}_x/\text{AC} \) and \( 5\text{VO}_x/\text{AC} \) and a mixture of \( \text{V}_2\text{O}_3 \) and vanadium carbide in \( 12\text{VO}_x/\text{AC} \) sample). All \( \text{VO}_x/\text{AC} \) and \( \text{V}_2\text{O}_5 \) samples can dehydrogenate propane: bulk \( \text{V}_2\text{O}_5 \) already at 350 °C through the oxidative dehydrogenation pathway with lattice oxygen participation, whereas the crystalline VC is active above 485 °C through a non-oxidative pathway. Re-oxidation with \( \text{CO}_2 \) takes place above 570 °C.

### 3.3.5 Time Resolved Isothermal DRIFTS Experiments

Transient behaviour of \( \text{CeO}_2 \), \( \text{CeVO}_4 \) and \( \text{V}_2\text{O}_5 \) during isothermal reduction with propane and re-oxidation with \( \text{CO}_2 \) was investigated with an in situ DRIFTS analysis at 550 °C (Figs. 10, 11 and S11–S17). Only bulk oxides were analysed due to the black colour and total absorbance of all AC supported catalysts. No interaction of propane or \( \text{CO}_2 \) with \( \text{CeVO}_4 \) was observed and these results are consequently not shown.

Exposure of \( \text{CeO}_2 \) to propane (Fig. 10a) showed instantaneous formation of CO and \( \text{CO}_2 \) which decayed slowly with prolonging TOS. Also, a rapid increase of the broad polydentate carbonate bands (1454 cm\(^{-1}\)) was observed (Fig. S12). These carbonates are observed regularly over ceria and are thermally very stable, as bands remain stable during the re-oxidation experiment. Also, instantaneous formation of CO is observed; it goes through a maximum and slowly starts to decline after 300 s of \( \text{CO}_2 \) exposure. This confirms \( \text{CO}_2 \) dissociation and oxygen vacancy replenishment, leading to oxidation of \( \text{CeO}_2-x \). Existence of the band at 1765 cm\(^{-1}\) (CO adsorbed on reduced \( \text{Ce}^{3+} \) sites [28]) after 10 min of oxidation at 550 °C (Fig. S14) suggests oxidation of \( \text{CeO}_2-x \) with \( \text{CO}_2 \) does not proceed to completion.

Upon exposure of \( \text{V}_2\text{O}_3 \) to propane (Figs. 11a, S15 and S16), the V=O vibration overtones at 2005 and 1969 cm\(^{-1}\) diminish after 53 s, indicating surface reduction [29]. In parallel to propane introduction, the \( \text{CO}_2 \) signal (2340 cm\(^{-1}\)) lights off, goes through a maximum at 135 s

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**Fig. 10 a** Reduction of \( \text{CeO}_2 \) with propane and time resolved signal intensity changes for propane (2967 cm\(^{-1}\)), \( \text{CO}_2 \) (2340 cm\(^{-1}\)), \( \text{CO} \) (2180 cm\(^{-1}\)), and carbonates (1454 cm\(^{-1}\)). **b** Re-oxidation of \( \text{CeO}_2-x \) with \( \text{CO}_2 \) and time resolved signal intensity changes of \( \text{CO}_2 \) (2340 cm\(^{-1}\)), \( \text{CO} \) (2180 cm\(^{-1}\)), and carbonates (1454 cm\(^{-1}\)). Please refer to online version of this manuscript for colour figure
and declines slowly. Formation of gas phase CO (characteristic band at 2180 cm$^{-1}$) is much smaller compared to CO$_2$ and appears only after the surface V=O overtone signal disappears at 100 s. This time-resolved experiment reveals the oxidation of propane to CO is possible only in the presence of a partly reduced surface, most likely containing V$^{4+}$. On the reduced V$_2$O$_3$ sample, the envelope of signals between 1300 and 1550 cm$^{-1}$ appears (Fig. S16A), which belong to gas phase propane; no carbonates are formed. Absence of bands above 1600 cm$^{-1}$ indicates no carboxylates or bicarbonates are formed.

Re-oxidation of V$_2$O$_3$ with CO$_2$ occurs only marginally, since only about 3% of initial V=O band intensity was achieved after 400 s of oxidation, Fig. 11b, S17).

To summarize, time resolved DRIFTS experiments showed that reduction of CeO$_2$ with propane at 550 °C is fast, and that instantaneous surface population with polydentate carbonates takes place. Re-oxidation with CO$_2$ is substantial, but does not proceed to completion. This suggests the working state of the CeO$_2$ catalyst during the propane-CO$_2$ reaction is partly reduced.

Reduction of V$_2$O$_5$ is slower (CO$_2$ peak intensity is reached 60 s after propane introduction, compared to 5 s for CeO$_2$), re-oxidation by CO$_2$ is negligible. This suggests a slow irreversible transformation of initially present V$_2$O$_5$ into V$_2$O$_3$. Also, the inability of V$_2$O$_4$ and V$_2$O$_3$ to dissociate CO$_2$ shows the crucial role of lattice oxygen (nucleophilic O$^{2-}$ species) for enabling the oxidative dehydrogenation reaction pathway for propene formation. These findings are in line with catalytic tests (stable activity and low propene selectivity over CeO$_2$, compared to fast deactivation and total loss of propene selectivity over V$_2$O$_3$).

3.3.6 Raman Analysis

In the fresh and spent 2VO$_x$/AC and 5VO$_x$/AC catalysts, no signal below 1000 cm$^{-1}$ is visible (Fig. 12a). This is due to the absence of V=O bonds in these samples and shows that only vanadium carbide (VC) is present [30]. Also, the VC phase is resistant towards oxidation during propene-CO$_2$ ODH reaction, thus eliminating this possibility for the observed catalyst deactivation (Table 1). In the fresh 12VO$_x$/AC sample, the bands at 996, 700, 529, 478, 410, 287 and 142 cm$^{-1}$ are visible, which is consistent with the presence of V$_2$O$_3$ [31]. This is in line with the XRD results (Fig. 5a).

The formation of newly formed V$_2$O$_{13}$ phase is likely related to exposure of finely dispersed V$_2$O$_3$ to highly reducing conditions during the propane-CO$_2$ ODH reaction.

In the CeVO$_4$/AC samples (Fig. 12b), only characteristic CeVO$_4$ Raman bands appear at 217, 257, 369, 463, 775 and 845 cm$^{-1}$ [14]. In the fresh 30CeVO$_4$/AC and 40CeVO$_4$/AC samples, weak bands at 998 and 705 cm$^{-1}$ are visible, which suggests presence of V$_2$O$_3$ in these samples. Their fraction is very likely minor, as they could not be identified through XRD.

4 Discussion

The initial propene selectivity of CeO$_2$/AC catalysts is low (16–27%) and stabilizes after 60 min of reaction at notably higher values (38–50%, Table 1). The re-oxidation of small
CeO$_{2-x}$ crystallites (4 nm), as present in CeO$_2$/AC catalysts with CO$_2$, occurs at higher temperatures compared to bulk CeO$_2$ (15 nm), revealing it is more difficult to dissociate CO$_2$ as the CeO$_2$ size decreases (Fig. 9a). This is consistent with structure sensitivity for CO$_2$ activation, namely the π-bond in C=O and TOF increases with increasing particle size, as a certain degree of site coordination is required [34, 35].

The propene selectivity appears to be influenced by the oxidation degree of CeO$_{2-x}$. Lower abundance of reactive surface oxygen sites in partly reduced CeO$_{2-x}$ crystallites, when supported over AC compared to bulk CeO$_2$, provides less active sites for the activation of the C=C bond in propene. Consequently, higher propene selectivities are achieved over nanosized CeO$_{2-x}$.

Nowicka et al. [17] ascribed the initial deactivation of Pd/CeAlO$_x$ catalysts and a concomitant propene selectivity increase to the consumption of reactive oxygen species stored within the ceria lattice. These authors also suggest that the nonselective oxygen species, which are likely electrophilic, are singly charged interstitial oxygen anions. Once these O$^-$ species are consumed, the catalyst can be re-oxidized by CO$_2$.

The fast deactivation and complete loss of propene selectivity over bulk V$_2$O$_5$ is related to its quantitative reduction from V$^{5+}$ to V$^{3+}$, which leads to a progressive shift from propane ODH to propane cracking reaction. The CO$_2$-TPO experiment (Fig. 9c) revealed that bulk V$_2$O$_5$ cannot be re-oxidized by CO$_2$ at 550 °C. This shows the participation of CO$_2$ in the propane ODH reaction is negligible and the dominant ODH reaction pathway is governed by the availability of lattice oxygen in V$_2$O$_5$ and V$_2$O$_4$.

The reduction and re-oxidation dynamics of CeO$_2$ and V$_2$O$_5$ differ considerably, as could be observed by transient isothermal DRIFT spectroscopy analyses (Figs. 10 and 11). Propane interaction with CeO$_2$ leads to instantaneous and simultaneous CO$_2$ and CO formation which tail off slowly. Such behaviour is likely connected to the diffusion of lattice oxygen from the bulk to the surface [36], where it participates in the oxidation reactions.

Upon re-oxidation of CeO$_{2-x}$ with CO$_2$, the polydentate carbonate signal stabilizes after 10 s of CO$_2$ addition, suggesting a kinetic preference for these species. The instantaneous appearance of a CO signal confirms facile CO$_2$ disproportionation and catalyst re-oxidation at 550 °C.

During V$_2$O$_5$ reduction with propane, the CO$_2$ signal lights off slowly and reaches a maximum at about 70 s after propane introduction. This suggests higher propane oxidation rates with lattice oxygen of CeO$_2$ compared to V$_2$O$_5$, which correlates also with notably higher initial propene selectivity over bulk catalysts (10% over CeO$_2$ and 27% over V$_2$O$_5$). CO appears after V=O overtone vibrations disappear (suggesting the absence of V$^{5+}$ on the surface) [37].

At higher vanadium loadings in the VO$_x$/AC catalysts (12 wt%), a separate V$_2$O$_1$ phase is formed which is inert towards CO$_2$ and does not promote propane dehydrogenation. All VO$_x$/AC catalysts exhibit some deactivation with TOS, but propene selectivity remains constant (Table 1). Also, CO was identified as the reaction product during the entire duration of the catalytic tests and its concentration followed that of propene (Fig. S18), whereas the concentration of all other reaction products remained stable. This suggests that propene and CO are produced by the same oxidative dehydrogenation pathway (reaction 1). Considering that the fresh and spent catalysts contains no lattice oxygen (TEM-SAED, XRD and Raman analyses confirm a VC phase is formed exclusively at vanadium loadings up to...
we can postulate that CO₂ activation over the VC crystals is assisted by the adsorbed propane (protons at the methylene and methyl positions). In the absence of these electrophilic species which facilitate CO₂ decomposition [38] and H₂O formation, CO₂ activation requires temperatures close to 600 °C (Fig. 9c), which is above the reaction temperature used in this work. The deactivation of VOₓ/AC catalysts is accompanied by a stable propane selectivity, which indicates that the total number of active sites, and not their nature, is changed with TOS. Oxidation of the VC phase during the propane-CO₂ ODH reaction does not occur, due to absence of V–O bonding in Raman spectra of the spent 2VOₓ/AC and 5VOₓ/AC catalysts. As a result, deactivation is probably related to blocking of active sites by carbon. Recently, Thakur et al. [39] report of in situ formation of oxycarbide phases (V₂O₃ and V₈C₇) during exposure of vanadium containing MXene catalysts to CH₄ and CO₂ atmosphere at much higher temperatures (800 °C).

The CeVO₄/AC catalysts showed the highest catalytic performance in terms of propane yields. Upon dispersion of CeVO₄ over activated carbon, a thin (1–2 nm) amorphous phase is formed over the CeVO₄ crystals. Its formation is likely connected to calcination in argon. The amorphous layer is intrinsically defective and the reactivity of oxygen in amorphous mixed metal oxides is higher than in any of its crystalline components [40]. Ruth et al. [41], report that the amorphous part of the multiphase Mo–V–Nb oxide catalyst is particularly important during oxidative dehydrogenation and partial oxidation of ethane.

During oxidative dehydrogenation of ethane, a transformation of VOₓ/CeO₂ to CeVO₄ was identified by Martinez-Huerta et al. [14]. Based on the operando Raman analysis of the catalyst’s structure, they identified the bridging oxygen atom (Ce–O–V) present in the ill-defined CeVO₄ phase as the active site for the rate determining step in the ODH reaction. Exposure to reaction temperatures above 500 °C favours crystallization of the CeVO₄ phase, making it inactive in the ODH reaction [14].

An increase of propane ODH catalytic activity scaled with the CeVO₄ loading. Catalytic activity is in line with the reox ability of the supported CeVO₄ phase, probed by propane and CO₂ (Figs. 8 and 9), which revealed lattice oxygen abstraction and re-oxidation are feasible under the reaction conditions. TEM analysis of the CeVO₄/AC catalyst after reaction revealed elimination of the amorphous CeVO₄ layer and the deposition of a few layers of carbon on the surface. This change is likely correlated to the observed catalyst deactivation. Since propane selectivity does not alter drastically with TOS (Figs. 2 and 3) despite notable deactivation, the number and not the nature of the active sites is decreased. A recent review of propane ODH with CO₂ by Atanga et al. [5] suggests that indium and especially gallium based catalysts are superior in activity and selectivity compared to chromium, platinum and vanadium based ones. When benchmarking the performance of best performing sample in this work (30CeVO₄/AC, 15.3% C₃H₆ conversion, 42% C₂H₄ selectivity, 6.4% C₂H₆ yield, C₃H₆ productivity of 9.5 × 10⁻⁵ mol/(gcat min) at 550 °C, Table 2) with those reported over Ga₂O₃/Al₂O₃ by Michorczyk et al. [42], at 550 °C. A similar initial activity was observed (18% C₃H₈ conversion), but C₂H₄ selectivity was much higher (90%), corresponding to C₃H₆ productivity of 7.2 × 10⁻⁵ mol/(gcat min). Xu et al. [43] tested several supports (TiO₂, SiO₂, ZrO₂ and MgO) for dispersing the active Ga₂O₃ phase. At 600 °C, the most active was Ga₂O₃/Al₂O₃, which enabled 26% conversion at 94% C₃H₈ selectivity, resulting in C₃H₆ productivity of 11.2 × 10⁻⁵ mol/(gcat min).

Chen et al. [44] investigated how different supports (Al₂O₃, SiO₂ and ZrO₂) influence the propane ODH activity of 10 wt% In₂O₃ phase. At 600 °C, the highest propane selectivity of 85% was obtained In₂O₃/Al₂O₃ catalyst at a propane conversion of 20%, resulting in a propene productivity of 5.6 × 10⁻⁵ mol/(gcat min).

Based on the above, the propane selectivity of best catalyst (30CeVO₄/AC) in this work is about twofold lower compared to those of Ga₂O₃ or In₂O₃ catalysts, but propene productivities are comparable.

5 Conclusions

The re-oxidation of small CeO₂₋ₓ crystallites (4 nm) with CO₂ occurs at higher temperatures compared to bulk CeO₂ (15 nm), revealing it is more difficult to dissociate CO₂ as the CeO₂ size decreases. Catalyst reduction by propane and re-oxidation by CO₂ are fast under reaction conditions and the propane dehydrogenation reaction proceeds via lattice oxygen participation. The Main reaction pathway over cerium containing catalysts is the total oxidation of propane.

Under propane-CO₂ ODH reaction conditions, V₂O₅ is irreversibly reduced to V₂O₃, which leads to a progressive shift from propane ODH to the propane cracking reaction. The participation of CO₂ in the ODH reaction is negligible and the reaction pathway is governed by the availability of lattice oxygen in V₂O₃ and V₂O₅. V₂O₃ preferentially catalyses propane cracking.

In the VOₓ/AC catalysts, a VC phase is formed exclusively at vanadium loadings up to 5 wt%, whereas VC and V₂O₅ coexist at 12 wt% vanadium loading. By combining the C₃H₆-TPR, CO₂-TPO, and catalytic results we can postulate that CO₂ activation over the VC crystals is assisted by the adsorbed propane. As a result, the propane-CO₂ ODH reaction, over vanadium carbide, proceeds through...
the Langmuir–Hinshelwood mechanism. The deactivation of VOx/AC catalysts is accompanied with a stable propane selectivity, which indicates the total number of active sites and not their nature is changed with TOS. Oxidation of the VC phase during the propane-CO2 ODH reaction does not occur due to the absence of any V–O bonding in spent catalysts. As a result, deactivation is probably related to blocking of the active sites by carbon.

The active site for the propane ODH reaction in the CeVOx/AC catalysts is a thin (1–2 nm) amorphous CeVOx phase which covers the CeVOx crystals. Propane and CO2-TPR experiments confirmed that during the propane ODH reaction lattice oxygen abstraction and re-oxidation are feasible, indicating active participation of CO2 and a Mars van Krevelen reaction mechanism. During reaction, crystallization of the amorphous CeVOx layer and surface covering with carbon, which are the causes of catalyst deactivation.

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Compliance with Ethical Standards
Conflict of interest The authors declare no conflict of interest.

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