# Support Effects in Vanadium Incipient Wetness Impregnation for Oxidative and Non-oxidative Propane Dehydrogenation Catalysis

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**Abstract:** Oxidative propane dehydrogenation with carbon dioxide (OPDH) is an attractive technology, co-producing carbon monoxide and propylene with a potentially negative greenhouse gas balance. Vanadium oxide containing materials are a promising class of catalysts for such process. In this study we introduce vanadium into a range of micro- and mesoporous aluminosilicate materials by incipient wetness impregnation with NH<sub>4</sub>VO<sub>3</sub> and the complexing agent oxalic acid, targeting a surface density of 0.6 V atoms per nm<sup>2</sup> of pristine support. Aspects of this impregnation procedure and its interaction with the support are discussed in the context of potential sources of variability in the dispersion of VOx species within the catalyst materials. The results indicate no formation of a monolayer of vanadium species, and differences in catalyst dispersion are discernible through comprehensive characterization techniques, including thermogravimetric analysis (TGA), X-ray diffraction, Raman spectroscopy, H<sub>2</sub>-TPR and UV-Vis spectroscopy. The materials are evaluated for the catalytic CO<sub>2</sub>-assisted propane dehydrogenation in two pressure regimes while being compared to classic non-oxidative propane dehydrogenation (PDH). Results are analyzed using a multivariable analysis of reactants and products, which provided valuable insights for catalyst design. The larger pore material with few acid sites (MCM-41 with Si/AI = 180) demonstrates the highest activity in terms of PDH and high pressure OPDH, i.e. high propane conversion and quasi equivalent propylene production with similar CO<sub>2</sub> co-conversion and CO co-production). Yet, in terms of responding to the introduction of CO<sub>2</sub>, the zeolites seem to respond better in terms of producing less H<sub>2</sub> for only a small decrease in propylene. These microporous materials, except for the most acidic aluminous BEA, exhibit significant increase in their production rates when increasing the total pressure in OPDH.

Key words. Oxidative propane dehydrogenation, CO<sub>2</sub>, incipient wetness impregnation, propylene, vanadium oxides

# 1. Introduction

Alternative routes for propylene production are sought after for commercial and environmental motivations. Propylene is a critical component in plastics production and a fundamental building block for various essential chemicals, but global production capacity is well below the economic optimum<sup>1</sup>, and production largely derives from FCC and steam cracking (around 60-70%)<sup>2-4</sup>. In addition, the average CO<sub>2</sub> emissions associated with global propylene production is 2.1-2.5 kg<sub>CO2-eq</sub> kg<sub>C3H6</sub><sup>-1,5.6</sup> The development and implementation of additional, less CO<sub>2</sub>-intensive production capacity is therefore desirable<sup>4,7,8</sup>. Dedicated propylene production through direct propane dehydrogenation (non-oxidative) is being expanded commercially and can realize an estimated 1.6 kg<sub>CO2-eq</sub> kg<sub>C3H6</sub><sup>-1</sup>. Further process and catalyst improvements for the non-oxidative route are active areas of development,<sup>9,10</sup> but an alternative route using a sacrificial oxidant, and producing H<sub>2</sub>O instead of H<sub>2</sub> (oxidative propane dehydrogenation (OPDH)) also attracts interest.

Traditionally the oxidant of choice is  $O_2$ , but the use of  $CO_2$ , a softer oxidizing agent, can provide additional benefits. Alongside the reduction in coke formation,<sup>1,11</sup> co-consumption of a greenhouse gas and the value-added co-production of CO are achieved. This can be achieved either indirectly (*i*-OPDH) via the consumption of hydrogen produced in dehydrogenation, or directly (*d*-OPDH) with  $CO_2$  replenishing catalyst oxygen used up for dehydrogenation. For minimal greenhouse gas emissions, an ideal mechanism overall consumes equal moles of  $CO_2$  and propane,<sup>12</sup> which can be reached by d-OPDH. Moreover, in the oxidative pathway alternatives to environmentally problematic chromium,<sup>13</sup> or costly platinum used in traditional PDH catalyst may be viable<sup>6,10</sup>. Catalyst improvement is an outstanding challenge for performant d-OPDH. Promising results have been achieved with supported vanadium oxide (VO<sub>x</sub>) materials, although in that study, the role of the support was not studied, and a benchmark  $\gamma$ -alumina was taken<sup>12</sup>.

Here, we explore the impact of the support structure and the metal(oxide)-support interactions in VO<sub>x</sub>-catalyzed OPDH with a focus on both  $CO_2$  and propane conversion. The dissociative adsorption of propane with C-H scission is accepted as the rate limiting step with industrially used Cr and Pt PDH-catalysts. Still, there is no complete consensus about the heterolytic or homolytic nature of the mechanism<sup>14</sup>. OPDH is mostly described according to a Mars Van Krevelen mechanism<sup>15,16</sup> where the propane is oxidized by surface oxygen with metal reduction, which is subsequently reoxidized by accepting oxygen onto the surface from the oxidizing agent. A goal

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in OPDH catalyst development is to increase the contribution of the OPDH pathway (producing  $H_2O$ ) versus the DPH pathway (producing  $H_2$ ) while maintaining propylene selectivity. One avenue is tuning the interactions between the vanadium species and the support to optimise oxygen exchange by the solid catalyst<sup>17</sup>. Also, the nuclearity of the vanadium clusters or chains on the surface seem to play a role, which can be manipulated through vanadium loading and dispersion. A relevant challenge is therefore to control the degree of inorganic polymerization<sup>18</sup>. For microporous (or small mesoporous < 5 nm) supports, the metal deposition method affects the VO<sub>x</sub> dispersion and polymerization (from monomers and dimers to layers and nanoparticles), and eventually the predominant embedding of vanadium in or outside the pore system.

Incipient wetness impregnation (IWI) is the simplest and most cost-effective method for introducing metals into porous supports<sup>19–21</sup>. Nevertheless, controlled IWI is not straightforward, depending on case specific properties such as metal precursors, pH<sup>22</sup>, point of zero charge (PZC)<sup>18,23</sup>, support structure<sup>24</sup> and particle size. We apply classical incipient wetness impregnation with NH<sub>4</sub>VO<sub>3</sub> onto various supports, using oxalic acid as a complexing agent. We provide a concise overview of the chemical process, from the initial solution preparation to the immobilization of the metal, emphasizing technical intricacies of this catalyst preparation method. From a diverse set of supports we yield valuable insights for the future development of vanadium-supported materials

## 2. Experimental section

# 2.1. Catalyst impregnation

A selection of catalytic materials with varying pore sizes and structures was chosen for this research. The selected structures included mesoporous materials (MCM-41), micro and mesoporous materials (Faujasite-FAU, Beta-BEA), and small-pore zeolite (Chabazite-CHA). The molar ratio of Si/AI, as determined by ICP, is indicated at the end. MCM-41-15 and MCM-41-180 were procured from Nankai University Catalyst Co. Ltd, FAU-40, BEA-20, and BEA-150 were obtained from Zeolyst.

Interzeolite Conversion (IZC) starting from CBV780 and a mixture of molar proportion  $1SiO_2:0.025AI:0.35TMAda:0.35OH\neg-:12.5H_2O$  and CBV780 (US-Y, Si/AI = 40) produced the CHA30<sup>25–27</sup>. The synthesis was carried out in 23 ml teflon cups in stainless steel autoclaves (acid digestion vessel 4749, Parr Instruments). The autoclaves were heated in a mechanical convection oven (Heratherm, Thermo Scientific) under 600 rpm internal stirring (heat-resistant multi-position stirring plate, 2 mag) or under tumbling at the corresponding synthesis temperature. After cooling, centrifugation separated the solid phase from its synthesis liquor (6000 rpm,  $\ge 5$  min, Thermo Fisher Scientific SL16). The samples were washed with deionized water ( $18.2 M\Omega \cdot cm^{-1}$ ) until the supernatant showed a pH below 9. The samples were dried overnight at 60 °C before further treatment. Calcination was performed at 580 °C for five hours reached at a ramp of 1 °C·min<sup>-1</sup> in a muffle furnace to remove the organic OSDA.

The Incipient Wetness Impregnation method (IWI) achieved vanadium metal deposition. The impregnation was carried out on all materials in the H<sup>+</sup> ionic form, except for BEA20, which was in the ammonium form (NH<sub>4</sub><sup>+</sup>). The impregnation volume for each material was pre-determined experimentally by adding water. Surface area analysis was conducted using the N<sub>2</sub>-adsorption and applying the BET model. We changed nominal loading to obtain the same theoretical or apparent vanadium superficial density<sup>28,29</sup> of 0.6 V<sub>atoms</sub>-nm<sup>-</sup><sup>2</sup> across different materials. At various concentrations, the ammonium vanadate solution was prepared with double the amount of oxalic acid per gram of ammonium vanadate (equivalent to a 2.6 molar ratio of oxalic acid to vanadium). The solution was subjected to 20 minutes of ultrasonic treatment until a deep blue colour fully developed. Without thermal treatment, a portion of the material was analyzed using TGA. Subsequently, air calcination was applied to the materials, involving a temperature ramp up to 600°C, followed by an isothermal hold for 8 hours.

## 2.2. Catalyst characterization

The elemental analysis was performed using an inductively coupled plasma-atomic emission spectrometer (ICP-AES, PerkinElmer Optima 3300 DV) with signals for V, AI, and Si at 292, 396, and 251.6 nm, respectively. Samples were digested in the acid mixture (HF/aqua regia). After a few hours, it was neutralized with 5 mL boric acid solution (0.49 M) and diluted to 20 mL in deionized water. An aliquot was diluted in a nitric acid (HNO<sub>3</sub>) solution.

The structure and crystallinity of the zeolites were confirmed by X-ray powder diffraction (P-XRD) on a high-throughput STOE STADI P Combi diffractometer in transmission mode with focusing Ge(111) monochromatic X-ray inlet beams ( $\lambda$  = 1.5406 Å, Cu K $\alpha$  source). Porosity was measured by nitrogen physisorption (Tristar II 3020, micrometrics) at 77 K on dried samples (16 h at 300 °C under N¬2). The relative nitrogen pressure varied between 0.01 and 0.99 (p/p0). The t-plot method (Harkins and Jura) was used to determine micropore volumes on the adsorption branch. The model of BET analysis was used to determinate the surface area.

Apparent Vanadium Surface density = 
$$\frac{N\nu}{S_{BETo}}$$
 Equation 1<sup>29,30</sup>

Where Nv is the number of vanadium atoms per gram of catalyst determinated by ICP (atoms  $\cdot g^{-1}$ ) and  $S_{BETo}$  is the catalyst specific surface area without impregnation, in m<sup>2</sup>.g<sup>-1</sup>, leading to atoms(V).nm<sup>-2</sup>.

SEM analysis was performed on the Jeol JSM-6010LV microscope at an acceleration voltage of 15 kV. Zeolite samples were attached to a piece of carbon tape. Subsequently, an electron conducting Pd/Au (60/40 ratio) layer was deposited on the samples.

Temperature-programmed reduction with  $H_2$  ( $H_2$ -TPR) and carbon dioxide temperature desorption (CO2-TPD) were carried out using an AMI-300 system from Altamira Instruments. For  $H_2$ -TPR, The samples (50 mg) were pretreated at 400 °C to remove adsorbed moisture and impurities. Afterwards, the flowing gas stream was switched to ultra-high purity He upon further cooling to 20 °C. Then, a 5%  $H_2/N_2$  flow (25 ml min<sup>-1</sup>) was passed over the catalyst bed while the temperature was ramped up from 100 to 800°C at a heating rate of 10 °C min<sup>-1</sup>. A thermal conductivity detector (TCD) monitored the hydrogen consumption signal. Before the outlet gases enter the TCD, a cooling trap was used to remove  $H_2O$ . The basicity of the samples was determined by CO<sub>2</sub>-TPD. Prior to the tests, the samples were outgassed under a helium flow (25 mL min<sup>-1</sup>) with a heating rate of 10 °C min<sup>-1</sup> up to 150 °C and kept at this temperature for 120 min. After cooling to 40 °C, an CO<sub>2</sub> flow of 25 ml·min<sup>-1</sup> was passed through the sample for 40 min. we flowed helium at 100 °C for 5 min, the CO<sub>2</sub> desorption was determined by increasing the temperature with a heating rate of 10 °C min<sup>-1</sup> up to 650 °C. The CO<sub>2</sub> in the effluent helium stream was measured with a thermal conductivity detector (TCD).

We measured the weight loss of spent catalysts with a TGA/DSC 3+, mettler toledo, following an  $N_2/O_2$  temperature ramp to discriminate between Water, soft and hard coke contributions, reported in the literature<sup>31</sup>. Water desorption accounts for the weight drop during a ramp from r.t. to 200 °C at 10 °C min<sup>-1</sup> flowing N<sub>2</sub> and isothermal conditions for 10 min. The subsequent weight drop is attributed to soft coke and occurs when we raise the T to 600 °C at 5 °C min<sup>-1</sup>. Hard coke results from the final variation in weight when under isothermal conditions at 600 °C we switch to O<sub>2</sub> gas for 30 min.

Raman spectroscopy was recorded on a Bruker Vertex 70 FTIR spectrometer, coupled with a Ram II. Raman module using a 1064 nm laser. For each sample, 1024 scans were collected at a resolution of 2cm<sup>-1</sup> and with the laser output set at 400mW.

# 2.3. PDH and CO<sub>2</sub>-ODHP reaction

The catalysts were pressed and sieved to 125-250  $\mu$ m to avoid internal mass transfer and temperature gradient limitations. The reactor comprises a packed-bed hastelloy-x reactor (ID 3.5 mm) loaded with 0.2000+/-0.002 g of catalyst. The bed was diluted with SiC (350  $\mu$ m) in the isothermic central zone and 4 grams of SiC was also added below and above the catalytic layer. After the reaction, the reactor content was sieved to recover the spent catalyst from SiC for further analysis. A Thermo Scientific Trace 1300 GC, with a TCD detector (Haysep N 60-80 0.25 m, Rt-XL Sulfur 60-80 1 m, Molsieve 5 Å 60-80 2 m, He carrier) and a FID (CP-PoraPLOT Q 25 m, N<sub>2</sub> carrier) analyzed the absolute gas composition using N<sub>2</sub> as an internal standard to calculate the outlet flowrate. Water and coke formation were derived from oxygen and carbon molar balances and reported in terms of molar flow rates.

In a standard catalytic test, 100 Nml·min<sup>-1</sup> (normal conditions defined at 1 atm, 0 °C) of the gas mixture flow  $CO_2/C_3H_8/Ar/N_2$ (2.5/2.5/45/50) was fed. Before catalytic testing, an activation procedure was followed, raising the temperature from room temperature to 600 °C at 1°C min<sup>-1</sup> at 6 bar. (GHSV =  $3.0E^{+4}$  Nml ml cat<sup>-1</sup>·h<sup>-1</sup>, WHSV =  $1.5 g_{propane} g_{cat}^{-1}\cdoth^{-1}$ ,  $1.5 g_{CO2} g_{cat}^{-1} h^{-1}$ ). The next three steps were isothermal time on stream (TOS) reactions. The first is classical PDH conducted at 6 bar. The last two stages were OPDH conducted at 0.6 and 6 bar. Between each step, the catalyst was regenerated by air (10ml·min<sup>-1</sup>,60 min) at 600°C.

To calculate the consumption rates of reactants and the production rates of main and side compounds, the N<sub>2</sub> flow was used as an internal standard. Additionally, the next equations define our use of conversion of component i (X<sub>i</sub>), selectifity for component j (S<sub>j</sub>), yield of propylene ( $Y_{C3H6}$ ) and space time yield of propylene ( $STY_{C3H6}$ ):

$$X_{i} = \frac{F_{i}^{IN} - F_{i}^{OUT}}{F_{i}^{IN}}$$
Equation 2  
$$S_{j}^{HC} = \frac{\vartheta_{j} F_{j}^{OUT}}{\sum_{j}^{HC} \vartheta_{j} F_{j}^{OUT}}$$
Equation 3  
$$Y_{C3H6} = \frac{F_{C3H6}^{OUT}}{F_{C3H8}^{IN}}$$
Equation 4

$$STY_{C3H6} = r_{C3H6} = \frac{r_{C3H6}}{w}$$
 Equation 5

Where  $F_i$  is the molar flow of i at the reactor (IN) and outlet (OUT) inlet, measured during the reaction in mol.h<sup>-1</sup>, r is reaction rate in mol·h<sup>-1</sup> kg<sub>cat</sub><sup>-1</sup>, and w is mass of catalyst in kg.

Given the presence of multiple reactions, including coke formation and propane dry reforming, we define the reaction's propane selectivity based on a carbon atom basis. Dry reforming,  $F_{CO}^{OUT} \ge F_{CO2}^{IN} - F_{CO2}^{OUT}$  and some other reactions have  $S_{CO} = F_{CO}^{OUT}/(F_{CO2}^{IN} - F_{CO2}^{OUT}) > 1$ . We therefore distinguish the source of CO by the molar balance between propane and CO<sub>2</sub>:  $F_{CO}^{from \, propane} = F_{CO}^{OUT} - (F_{CO2}^{IN} - F_{CO2}^{OUT})$  and  $F_{CO}^{from \, CO2} = F_{CO2}^{IN} - F_{CO2}^{OUT}$  and we define:

$$S_{reaction}^{propane} = \frac{reaction}{\sum_{j}^{HC} \vartheta_{j} F_{j}^{OUT} + F_{CO}^{from propane} + F_{coke}}$$
 Equation 6

Where  $S_{reaction}^{propane}$  is the overall selectivity of propane towards the "*reaction*" = (O)DHP =  $3 F_{C3H6}^{OUT}$  "oxidative" is in parenthesis as we cannot infer the mechanism (direct or indirect); cracking =  $F_{CH4}^{OUT} + 2 F_{C2H4}^{OUT}$ , reforming =  $F_{C0}^{from propane}$ , coking =  $F_{coke}$  and all the remaining *j* species as "others" =  $\sum_{i}^{NC} \vartheta_{ij}$ ,  $F_{ji}^{OUT}$  (hydrogenation of ethylene to ethane, cyclization or propane, propyne, propadiene, 1,3-butadiene and other C<sub>4</sub> HC).  $F_{coke}$  is derived from the deficit in the C-mass balance.

Activity profiles of the materials, depending on the chemical species as rates consumed or produced, were plotted in the interquartile analysis, also known as a box plot. This graphical representation displays the distribution of activity data, highlighting measures of central tendency (average activity) and the activity range in time during the experiment. In a box plot, a rectangle (the "box") is drawn to cover the interquartile range of activity (IQR) between the first and third quartiles of the experiment. Within the box, a line (-) is plotted to represent the median. Then, "whiskers" (labelled as o and  $\nabla$ ) extend from the box to the extreme values, pointing to the initial(o) and final activity ( $\nabla$ ). In the context of our study, interquartile analysis serves to partition the experiment's activity into distinct segments, with the interpretation differing according to the test conditions. For TOS experiments, each interquartile signifies the material's activity over a 50-minute timeframe (1/4 of total TOS at 600 °C) (further information is found in Fig. S1-2.).

Percentage relative change of various variables (here generically *a*) are denoted in this work as follows to evaluate data independently of absolute values:

$$\% \Delta a = \frac{(a_i - a_o)}{a_o} x 100$$
 Equation 7

In our study, we applied this tool to investigate alterations in surface area resulting from impregnation and catalytic assessments. The naked support was chosen as reference( $a_0$ ) to evaluate the impact of metal load over the BET surface. We employed linear interpolation techniques between the experimental data points for experiments necessitating time-sampling correction, specifically in comparing PDH and OPDH or in evaluating pressure effects. After applying the normalized difference over each point, the average and standard deviation were calculated from the data set. Assuming equidistant data points at every 10 minutes of Time on Stream (TOS) and interpolating values between the experimental points, a dataset of n-1 data points was generated, in this case, 19 points with n as total data (generally n=20).

## 3. Results and Discussion

## 3.1 Catalyst preparation by Incipient wetness Impregnation (IWI) of NH<sub>4</sub>VO<sub>3</sub> using Oxalic acid

IWI of vanadium into supports has been reported frequently<sup>16,21,32–34</sup>. The aqueous chemistry of the vanadium, ammonia, oxalic acid system is complex<sup>35,36</sup>. The V<sup>5+</sup> species are partially reduced by oxalic acid to V<sup>4+</sup> species with the irreversible release of CO<sub>2</sub> in the gas phase. As a result a combination of anionic VOx oxalate complexes with V<sup>4+</sup> and V<sup>5+</sup> is formed in the solution. Vanadium oxide cations in the solution and in the complexes include pervanadyl (VO<sub>2</sub><sup>+</sup>) and oxovanadium(IV) (VO<sup>2+</sup>).<sup>37</sup> Equations 8-12 show the main complex forming reactions. The aqueous species interact with acid groups on the support in incipient wetness, with the material surface being partially protonated in acidic medium (for example through equations 13 and 14, although these are hypothetical). Yet, these interactions during IWI are hard to study. Together with the speciation in solution, the support material's pore size and surface charge will affect the rate of vanadium introduction by IWI, and thus a distinct dispersion and speciation.<sup>32,22,38</sup> The surface charge of aluminous zeolites is determined by the amount of tetrahedral aluminum and silanol defects but also the local pH change by the acidic oxalic solution.

Table 1. Reactions involved in incipient wetness impregnatio
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Reaction	Chemical equation	
Redox reactions	$2VO_2^+{}_{aq} + C_2O_4^{2\text{-}}{}_{aq} + 4H^+{}_{aq} \rightarrow 2VO^{2\text{+}}{}_{aq} + 2CO_{2\text{ g}} + 2H_2O_1$	Equation 8 39
Vanadium Oxalic complex (V)	$VO_2^+aq + C_2O_4^{2-}aq \leftrightarrow VO_2(C_2O_4)^-aq$	Equation 936
	$VO_2^+aq + 2 C_2O_4^{2-}aq \leftrightarrow VO_2(C_2O_4)_2^{3-}aq$	Equation 1036
Vanadium Oxalic complex (IV)	$VO^{2+}_{aq} + C_2O_4^{2-}_{aq} \leftrightarrow VO(C_2O_4)_{aq}$	Equation 1136
	$VO^{2+}_{aq} + 2 C_2O_4^{2-}_{aq} \leftrightarrow VO(C_2O_4)_2^{2-}_{aq}$	Equation 12 <sup>36</sup>
Potential Support interactions	$S-OH + H^+ \rightarrow (S-OH_2)^+$	Equation 13 <sup>21</sup>
at low pH: ion+ligand exchange	$(S-OH_2)^+ + [VO(C_2O_4)_2]^{2-} \rightarrow (S-O)_{2-x}[VO(C_2O_4)^{2-x}] + x(H_2C_2O_4)$	Equation 14 <sup>21</sup>

We track the formation of the vanadium oxalate complexes in the above system and their interaction with the support material using UV-Vis absorption spectroscopy (Figure 1 a) and thermogravimetric analysis (TGA) (Figure 1 b & c). Free in solution, V(V) salts form oligomers and polymers through condensation reactions. These may induce cluster formation on support materials and reduce dispersion. We are therefore interested in observing the role of oxalate as complexing agent, preventing vanadium aggregation. Figure 1 a illustrates the changing vanadium speciation after mixing  $NH_4VO_3$  with oxalic acid. The solution transitions from yellow to an intermediate green, and finally turns deep blue indicative of V(IV). Without physical stimulation this takes several hours to be completed. Applying ultrasonic treatment significantly accelerates the chemical reaction, which nears completion after 30 minutes (the time typically used before IWI).

The number of oxalic acid molecules consumed in vanadium reduction, and retained in the pore system of the impregnated material was tracked using thermogravimetric analysis (TGA) from the mass balance of oxidizable oxalate after IWI and the amount of oxalic acid originally added (2.6 moles per mole vanadium). As the only organic source, the weight loss between 200°C and 600° (see figure 1b) can be fully attributed to oxalate that was not consumed by the redox reaction (eq-8). Figure 1c shows the molar balance of oxalate divided between oxalate lost from the vanadium reduction reactions or decomposition due to other reactions in the IWI, and oxalate retained as complexing agent or in the solution absorbed by the porous material. For all support materials, at least one oxalic acid is consumed per V in the reduction, suggesting ample reduction can have taken place (eq-8 suggest one oxalic to reduce 2 V), to a sort of equilibrium (excess oxalic) value. While the deep blue color in the solution suggests V(IV) would be dominant, it is clear that after IWI, it is hard to draw conclusions on the state of V. The measured ratio of oxalate/vanadium in the materials after IWI ranges from 0.7-1.6 for most materials in this study, and this remaining organic fraction corresponds to ligated and aqueous oxalate. During a thermal treatment involving grafting with vanadyl isopropoxide, Love et al.<sup>40</sup> observed the elimination of organic ligands, leading to the formation of transient V–OH species. These transient species subsequently interacted with the silica surface, resulting in the creation of isolated, tetrahedral VO<sub>4</sub> sites. A similar behavior could be expected for the oxalic complex, e.g. during the heating in a post-IWI catalyst pretreatment. The final classic calcination these catalysts undergo after IWI will change or influence the oxidation state and speciation heavily from the post-IWI situation (see 3.3).

Yet, the ratio of oxalate ligands to vanadium is synthetically relevant because higher ligation degree results in bulkier complexes that have more difficulty entering and diffusing through porous supports (products of eq-10 and -12 vs those of eq-9 and -11). Adding large amounts of organic acid is thus beneficial to enhance dispersion (vanadate dissolution) in solution but may come at a cost of reduced penetration. An optimum therefore exists, which will depend on support characteristics. The support will influence the equilibrium abundance of vanadium oxidation states and complex ligation number through and in association with pH, ionic strength, temperature and introduced concentrations of NH<sub>4</sub>VO<sub>3</sub> and oxalic acid. In addition, it will influence the vanadium-support interaction through its surface chemistry and porosity steering surface dispersion and pore diffusion.



**Figure 1. A)** Spectrum of NH<sub>4</sub>VO<sub>3</sub> and oxalic acid solution under the usual concentration of IWI (approximately 0.05 M NH<sub>4</sub>VO<sub>3</sub>). (Orange), Fresh solution; (Green) after 30 minutes and (blue) after 30 minutes with ultrasonic treatment. (diluted 60x). **B)** TGA analysis over impregnated samples without thermal treatment. Loaded to a nominal apparent surface density of 0.6 atom·nm<sup>-2</sup>. TGA ramp of temperature to ambient-300°C (N<sub>2</sub>), isothermal 300 °C (15min, O<sub>2</sub>) 300 to 710 C (20 °C/min, N<sub>2</sub>), Intermediary step to cool down until 350·°C, 350°C to 710 °C (20°C/min, O<sub>2</sub>). **C)** analysis of the organic weight loss fraction compared to the V<sub>Nominal</sub> loaded.

## 3.2 IWI versus support texture

The impact of vanadium impregnation on textural properties was measured through  $N_2$  physisorption. The results are summarized in Figure 2 and Table 2 (see Figure S6 for the full isotherms before and after impregnation for all the materials). The preparations were succesful in targetting the 0.6 Vatom/nm<sup>2</sup> apparent surface density (see eq-1 for definition, Fig. 2 blue triangles), although the BET method has its limits (*e.g.* large cilindrical pores in MCM vs small pores with cages in CHA)<sup>41</sup>. The actual surface density cannot be reported because the vanadium dispersion across the surface cannot be assumed to be uniform. CHA-30, with the smallest pore size in the series, experienced the largest loss in surface area (Fig. 2, black bar), while MCM41-180, with the highest weight based V-loading, saw a reduction of approximately 20%. The cutoff for severe surface area loss (Table 2) seems to be between 0.55 nm (BEA) and 0.38 nm (CHA).



Supported V Catalyst

**Figurel 2** Left axis, black bar: Reduction in the surface area evaluated as the normalized difference compared to the surface area of the catalyst without impregnation. Right axis, red square: Vanadium loading determined by ICP after impregnation and calcination. Right second axis, blue triangle: Vanadium loading translated to apparent surface density according to eq-1.

		Pristine material			Vanadium Loading	Impregnated material After calcination		
Structure	Pore Size -nm-	Micropore volume (t- plot) cm³·g <sup>-1</sup>	Mesopore volume* cm³·g <sup>-1</sup>	BET Surface m²·g <sup>-1</sup>	(target)** mmol⋅g <sup>.1</sup>	Micropore volume (t- plot) cm <sup>3</sup> ·g <sup>-1</sup>	Mesopore volume cm <sup>3</sup> ·g <sup>-1</sup>	BET Surface m²·g <sup>-1</sup>
MCM-41-15	3.8	0.17	0.56	710	0.70 (0.70)	0.13	0.46	601
MCM-41- 180	3.8	0.23	0.72	1113	1.00 (1.11)	0.17	0.42	881
FAU-40	0.74 + mesopore	0.28	0.24	736	0.76 (0.73)	0.21	0.23	660
BEA-20	0.55	0.24	0.16	583	0.58 (0.58)	0.18	0.16	523
BEA-150	0.55	0.20	0.10	478	0.49 (0.47)	0.17	0.09	390
CHA-30	0.38	0.27	0.44	629	0.64 (0.62)	0.09	0.22	195

Table 2 Textural properties and their change under impregnation with a nominal target of 0.6 Vatom nm<sup>-2</sup>

\*The mesopore volume was calculated by subtracting the micropore volume from the total volume of N<sub>2</sub> adsorbed at P/P0=1. This means that in some cases a considerable amount of external surface is also included in this calculation (this is the case for FAU and CHA). However, since the external surface also acts as a potential site for V-species, we decide to include it. \*\*targeted loading to reach a apparent density of 0.6  $V_{atom}$ -nm<sup>2</sup>

#### 3.3 Reducibility and CO<sub>2</sub> adsorption over impregnated and calcinated samples.

The six materials with a vanadium loading of 0.6 atoms per nm<sup>2</sup> of surface area in the pristine support were further tested for their redox properties and interaction with  $CO_2$  in temperature programmed reduction (TPR) and – desorption (TPD) experiments. Both properties are mechanistically relevant for PDH and OPDH. Figure 4 illustrates the results of catalyst reduction using H<sub>2</sub> and CO<sub>2</sub> affinity from  $CO_2$  desorption profiles (also see Table 3). Most materials display a dominant single H<sub>2</sub> consumption peak around 544 °C indicating a uniformity in vanadium reducibility. H<sub>2</sub> consumption at higher temperatures and with lower H<sub>2</sub>/V ratios are likely due to partial reduction of clustered vanadium oxide<sup>42</sup>.



**Figure 3 A)** Temperature-Programmed Reduction (TPR) profiles. B) CO<sub>2</sub>-Temperature Programmed Desorption (CO<sub>2</sub>-TPD) profiles for the freshly calcined V-supported catalysts.

The catalysts with the largest pore sizes (the MCM-41 materials) display the highest  $H_2/V$  ratios, amounting to 1.2 and 0.83, respectively for the Si/Al 15 and 180 compositions. These results correspond with a model for vanadium IWI that depends on diffusion of complexes into the pore system wherein the presence of mesopores is greatly beneficial for dispersion. In addition, the mesoporosity seems to exert its most positive effect in combination with a low Si/Al ratio (more reducable V). The lowest  $H_2/V$  ratio was found for the support with the narrowest pores, CHA-30, with a value of 0.53 and with the  $H_2$  consumption maximum located at a higher temperature (550 °C). The low  $H_2$  consumption, along with a large full width at half maximum for the peak is indicative of lower vanadium dispersion. This further supports the link between vanadium dispersion in IWI preparation with support pore size. These findings are consistent with the decrease in specific surface area observed in the CHA30 zeolite (70% reduction), attributed to the constrained access to the smallpore crystal interior resulting from vanadium oxide based pore blockage (on the outside or inside of the crystals).

 $CO_2$ -TPD indicates the catalyst surface basic sites that are accessible by the  $CO_2$  molecule. This is of obvious relevance for catalysts intended for a process using  $CO_2$  as a reagent, although the  $CO_2$  adsorption properties give no direct insight in the ability to use  $CO_2$  as an oxygen source for OPDH. Conventionally, basic sites on a catalyst are categorized as weak, intermediate, strong, and very strong, corresponding to desorption temperature ranges of 20–150, 150–300, 300–450, and >450 °C, respectively. Zeolites characterized by smaller pores (BEA and CHA) here demonstrate that a significant part of their  $CO_2$  desorption only occurs at high temperatures (>450°C) in contrast MCM-41 and FAU-40. The distribution of basicity inferred from these TPDs are however quite broad.

V/support	H₂ TPR µmol⋅g⁻¹	H₂ TPR µmol⋅m²	H <sub>2</sub> molar consumption ratio H <sub>2</sub> /V	µmol CO₂.g⁻¹	total CO <sub>2</sub> molar desorption ratio CO <sub>2</sub> /V
MCM41-15	863	1.22	1.2	44.2	0.06
MCM41-180	858	0.77	0.83	33.0	0.03
FAU-40	580	0.79	0.76	25.6	0.03
BEA-20	340	0.58	0.58	29.4	0.05
BEA-150	342	0.71	0.61	41.0	0.08
CHA-30	299	0.48	0.53	33.1	0.05

### Table 3 Summary of H<sub>2</sub>-TPR and CO<sub>2</sub>-TPD



Figure 4 Raman spectra of the Vanadium loaded catalysts with Barium sulphate as a baseline.

Figure 4 completes the picture, as it confirms that the low vanadium loading on various supports did not lead to significant clusters, or 2D bulk species, as confirmed by Raman spectroscopy and XRD analysis (Figure S5). Raman spectra displayed characteristic V=O stretching bands, with a soft peak around 1035 cm<sup>-1</sup>, nearly obscured by signal noise in MCM41-15. Literature assigns bands at 995-996, 700-703, 530, 500-483, 400-406, 300-306 and 285 cm<sup>-1</sup> to bulk V<sub>2</sub>O<sub>5<sup>43</sup></sub>. To further validate the absence of bulk vanadia, Raman spectra for the bare supports (MCM41-180, CHA30 and BEA150) were compared to their respective unimpregnated samples (see figure S8). This led to conclude that features at 451, 468 and 480 cm<sup>-1</sup> correspond to the MCM41-180, CHA30 and BEA150 supports, and the features related to bulk vanadium species are absent. These results are in agreement with the XRD patterns. Notably, the distinct peaks associated with the crystallographic planes of V<sub>2</sub>O<sub>5</sub> (at 19.4°, 22.5°, 28.2°, and 33.2°) were absent in all impregnations, yet, this does not exclude the presence of small nanosized clusters invisible to XRD. The presence of a narrow peak in H<sub>2</sub>-TPR at approximately 544 °C provides compelling evidence supporting sub-monolayer coverage. However, in alignment with the theoretical predictions of Rozanka et al<sup>44</sup>, we do not dismiss the potential existence of a complex mixture comprising monomeric, dimeric, and oligomeric species. This mixture is likely formed in a less controlled manner due to the intricate unidimensional mesopores in MCM-41 or the tortuosity within micropore zeolites.

#### 3.4 Catalytic test: PDH vs OPDH and Pressure sensitivity in OPDH

Figure 5 depicts the standard experimental protocol used for all catalysts, applied to MCM41-180. The propane conversion and carbon dioxide conversion are presented on the left axis, while the selectivity on the right axis is expressed based on what happens to the propane, based on our previously reported method (Rigamonti et al.).<sup>12</sup>. The selectivity for propylene is indicated by the green color, i.e. the(O)DHP category. Reforming (dry) and cracking represent other paths to consume propane, respectively with production of CO+H<sub>2</sub> or methane + ethylene.After a ramp protocol in ODHP and regeneration, the following 3 stages are isothermal at 600 °C. Stage 2 shows pure PDH with a 47% propane conversion is found at the start (6 barg), which is still a bit away from the thermodynamic equilibrium (65%), and drops to around 32%. The formation of coke is nearly invisible, with cracking being the most significant side reaction during an overall selective propylene formation (94% of propane conversion via ODHP). Following the initial regeneration and exposure to  $CO_2$  +propane (1 barg), the conversion drops to 28%, reaching an almost steady state at around 15% conversion and a stable selectivity of about 85 %. The increase in pressure during the OPDH to 6 barg which is the final condition in Figure 5, results in a substantial increment in both conversion and selectivity, pointing at improved kinetics and to higher reaction orders in the reagents for the desired OPDH reaction mechanism(s). While the conversion still remains below the activity (for propane) for the non-oxidative

dehydrogenation in the second stage, the conversion of  $CO_2$  is quite high, seemingly following the activity decline. Note that during the OPDH ramp (e.g. stage 1 figure 5), the conversion of propane and  $CO_2$  are almost equal, and their gap widens starting from 560°C and above. It is also worth to note that in presence of  $CO_2$ , cracking is suppressed as a side-reaction and dry reforming (which uses  $CO_2$  as co-reagent) becomes more relevant. The complete experimental plots (as in Fig. 5) for the entire time-on-stream experiment of all materials are found in Figure S3 A-E.



**Figure 5** Catalytic Test on MCM-41-180: The test comprises four stages, including intermediary regeneration using air. The first stage involves a dynamic OPDH experiment with a temperature ramp at 5°C·min<sup>-1</sup>. The second stage operates under conventional PDH in steady state at 600 °C and 6 barg, with no CO<sub>2</sub> fed into the reactor. The third and fourth stages are steady state time-on-stream OPDH experiments at 600 °C , respectively conducted under low (1 barg) and high pressure (6 barg). All OPDH experiments were run at a CO<sub>2</sub>:propane ratio of 1. Ramp experiment running from 400 to 600 °C at 6 barg. 200.0(2) mg catalyst pelletized to 125-250  $\mu$ m granules. Feed gas mixture of CO<sub>2</sub>/C<sub>3</sub>H<sub>8</sub>/Ar/N<sub>2</sub> of 2.5/2.5/47.5/47.5 Nml min<sup>-1</sup>, GHSV 3.0E<sup>+4</sup> Nmlgas mlcat<sup>-1</sup> h<sup>-1</sup> and WHSV 1.5 gC<sub>3</sub>H<sub>8</sub> gcat<sup>-1</sup> h<sup>-1</sup>.

With few exceptions, these transitions and the response to the experimental stages are recurrent for all the materials evaluated here. The activity in terms of propane conversion for OPDH is lower than that for PDH under the same experimental conditions. Additionally, increments in activity, at the expense of profile stability, become evident at increased pressure during OPDH. Possible explanations for these observations are as follows: firstly, the introduction of  $CO_2$  allows a new species to compete for adsorption sites on the available catalytic area and they certainly have an affinity, as evidenced from  $CO_2$  desorption still occurring at temperature higher than 600 °C in the TPD (Fig. 3B). On the other hand, imposing higher pressure translates into a higher concentration of reactants within the confined reaction space of the crystal's pore (or the material's in case of non-crystalline MCM-41) and an increase in adsorbed species. This favors kinetics.

The method of plotting data in figure 5 does not allow an easy comparison if this were to be compared for our 6 catalysts. Consequently, for a more rigorous and comparative evaluation of these experiments, a time dependent multivariate analysis is provided by adapted box-and-whisker plots. This approach employs reaction rates (in mol.h<sup>-1</sup>kg<sup>-1</sup>cat) and should be interpreted from the top down: the circle portrays the initial rate of consumption (-r) or production (+r) of a given species, while its terminal state, i.e. rate at the end of the experiment is shown by an arrow head, i.e. at 200 min on stream. The average activity over the whole time is thus shown as a bicolored diamond, while the box represents the activity at 50 and 150 min of time on stream (TOS). The median activity is the horizontal line in the middle of the box (= rate at 100 min). Since the selectivity is quite stable (Fig. 5 and Fig. S1), our analysis focuses more on deactivation and the absolute levels of the rates. Figure S2 shows how different deactivation profiles correspond to their box-and-whisker plot and how easily these can be compared. Still, one can deduce selectivities by comparing both reactants and products, e.g. when propane consumption and propylene production (black and blue) match each other quite well, this infers high selectivity for OPDH. Furthermore, it elucidates the activities related to CO<sub>2</sub> consumption followed by CO production. Lastly, as the discerning proxies for dehydrogenation and cracking, hydrogen and methane production rates are respectively presented.



**Figure 6** Box-and-Whisker plots across all V-Supported Materials and conditions during 200 min TOS. Horizontal analysis refers to a comparison at the same stage of the experiment for different materials, while vertical comparison pertains to the same material. All OPDH experiments were run at a CO<sub>2</sub>:propane ratio of 1. Ramp experiment running from 400 to 600 °C at 6 barg. 200.0(2) mg catalyst pelletized to 125-250  $\mu$ m granules. Feed gas mixture of CO<sub>2</sub>/C<sub>3</sub>H<sub>8</sub>/Ar/N<sub>2</sub> of 2.5/2.5/47.5/47.5 Nml min<sup>-1</sup>, GHSV 3.0E<sup>+4</sup> Nmlgas mlcat<sup>-1</sup> h<sup>-1</sup> and WHSV 1.5 g C<sub>3</sub>H<sub>8</sub> gcat<sup>-1</sup> h<sup>-1</sup>.

For PDH (Fig. 6 top), we can arrange the materials in terms of the highest average propylene space time yield (rate): MCM41-180 > FAU-40 > MCM-41-15 > BEA-150 > CHA-30 > BEA-15. Applying the same interpretation to the materials in low pressure OPDH leads to smaller differences in activity profiles with the following ranking: FAU40 > MCM41-180  $\approx$  BEA-150  $\approx$  BEA20 > CHA30  $\approx$  MCM-41-15. Finally, for high pressure OPDH,following ranking is found: MCM41-180  $\approx$  FAU40 > BEA-150  $\approx$  BEA20  $\approx$  CHA30  $\approx$  MCM-41-15. It is also evident that the deactivation profiles for propane conversion and the production profile declines for propylene give rise to a more compressed box-and-whiskers (black and blue) for PDH than for the OPDH cases. This points to at least a partially different mechanism of deactivation (and perhaps also activation).

BEA-20 exhibited a pronounced propensity for deep dehydrogenation (leading to coke) in all three experiment stages. This is evidenced from its high hydrogen production relative to the propane conversion (so more hydrogen is formed than the extent of the PDH reaction) and from the limited selectivity for propane-to-propylene conversion (the blue and black box and whiskers are not in parallel). This leads to the conclusion that secondary reactions take place on propylene and other HC products, producing H<sub>2</sub>. This is further corroborated by the high coking selectivity in Fig. 3-C, which in itself was also evidenced by subsequent TGA analyses of the used catalyst (see

Figure 7-C). Methane production was also notably higher in this material, likely due to the favorable cracking on this quite acidic support (assuming some of the acidity remains after the VOx IWI). The BEA-180 with less intrinsic acidity suffers less cracking and coking.

It is noteworthy that CHA-30, although it delivers the lowest rates in the series, is not as bad as expected based on its considerably smaller surface area post IWI compared to all other materials and the slightly lower V-loadings per weight of material. In fact, the CHA activity profiles for the high pressure PDH and OPDH closely resemble those of MCM41-15, which boasts nearly four times the surface area post IWI. For the low pressure OPDH, the comparison is not valid. We hypothesize that these results are due to confinement effects at play and that the small pore system requires higher pressure to bring the reagents together. A well-tuned small pore zeolite with preserved high surface areas and well dispersed vanadium remains a promising candidate for further exploration.

The ratio of CO to propylene serves as a reference point for gauging the extent of the direct oxidative mechanism  $(d-OPDH)^5$ . Nevertheless, dry reforming also contributes to CO production (1 propane and 3 CO<sub>2</sub> react to 6 CO and 4 H<sub>2</sub>), making it evident that, in all cases, the production of CO exceeds the consumption of CO<sub>2</sub>. The presence of some type of reforming is easily seen in the PDH experiments as well, where CO is produced without CO<sub>2</sub> present and more H<sub>2</sub> is formed than propylene. The O for CO production in such case derives from the loss of the vanadyl (V=O) of the surface<sup>34</sup>. Despite this, dry reforming in OPDH is less detrimental to the process compared to other side-reactions such as coking or cracking which negatively impact a future process due to the need for separating undesirable minor products or regenerating accumulated carbon on the surface. Dry reforming produces CO and H<sub>2</sub>, products that are already present in sizeable amounts. In such context, CO production can be considered a desirable parameter for the catalyst, in which case MCM-41-180 and FAU-40 could be considered.

To assess the extent of the transition from PDH to OPDH for the 6 catalysts, an additional analysis is performed on the normalized differences between the rates at equivalent sampling times. The average rate difference for the changes in hydrogen and propylene production between stages 2 and 4 in Figure 5 is reported in Figure 7-A. For the MCM41-180 material, it is evident that there is a reduction of approximately 76% in processes contributing to hydrogen (the traditional mechanism of PDH and deep dehydrogenation) simultaneously with a 30% decrease in propylene production. The reduction in propylene production for the zeolites (FAU, BEA, CHA) remained consistenty lower, at around 17-18% than for the bigger pore MCMs. This indicates that the indirect path where  $H_2$  is produced via PDH and CO<sub>2</sub> then converts to CO via a reverse water gas shift, is less dominant in the zeolitic (sub 1 nm pore) supports.



**Figure 7. A)** Normalized diminution of activity assessed across the Time on Stream (TOS) for OPDH (6 barg) relative to the activity in PDH at 600°C (stage 4 versus stage 2). **B)** Normalized change in propane consumption and propylene production assessed across the Time on Stream (TOS) for OPDH at high pressure relative to the activity at lower pressure (stage 4 versus 3). For both A and B, the standard deviations represented by the +/- bars are related to the condition reproducibility at each experimental point. **C)** Coke analysis classified as hard (black) and soft coke (white) measured by TGA and compared to the micropore volume of catalyst after impregnation and calcination.

Using a similar analysis but with the normalized difference in propane consumption and propylene production rates, we assessed the effect of pressure on the catalysis, specifically comparing stages 3 and 4 of the experiment as depicted in Figure 7-B. This evaluation allows us to determine the sensitivity of the OPDH systems to the stimulus imposed by increased pressure. As the reaction fails to reach equilibrium, analyzing pressure sensitivity provides us with a partial kinetic insight (although conversions are too high for initial rate analysis) into the facilitation or suppression of target and side reactions. When the increase in the consumption of propane concurs with a similar increase in the production of propylene, the selectivity for dehydrogenation remains unaffected (case 1). When the increase of propane is not matched, it indicates collateral (side) reactions are stimulated over the primary reaction of interest (case 2). A third scenario is the reverse, i.e. propylene exhibits higher positive sensitivity to pressure than propane, in which case the increase in pressure mitigates side reactions. MCM41-180 and FAU-40 seem to be described by case 2 although the differences are small. BEA-150 is a clear case 2, and indeed, the OPDH selectivity on average decreases from 84 to 79 % (Fig. S3-D). Zeolite BEA-20 even shows a small decrease in propylene production at higher pressure, reinforcing the conclusion of its high tendency to form coke at the expense of (and sacrificing) propylene. Finally, MCM41-15 and CHA-30 seem to exert a case 3 behavior (although error bars for CHA are large) and pressure increases the (O)PDH selectivity.

Figure 7-C illustrates the analysis of the coke formed after Stage 4 of the catalytic protocol, categorized into soft coke and hard coke (depicted in black on the right axis). On the left axis (pink), pore size determinations are displayed for impregnated and calcinated materials. Notably, no direct correlation between coke formation and porosity is evident, emphasizing the pivotal role of other factors such as structural shape and composition in its development. Coke formation remained below 3% in MCM-41 and CHA-30. For MCM-41, this low percentage is attributed to the critical role played by the unidimensional channels, limiting molecule contact between channels, thereby reducing polymerization potential. Furthermore, the larger pore size potentially offers reduced molecular condensation. In contrast, the limited coke formation in the CHA zeolite with the smallest pore size suggests that shape selectivity might play a more significant role in catalyzing side reactions in this material than in others. FAU-40, BEA-20, and BEA-150 structures exhibited coke formation ranging between 6-10 %. Particularly, the analysis of BEA-20 confirms its high propensity for polymerization, consistent with the negative effect with increased pressure and its deep dehydrogenation potential (H<sub>2</sub> formation in Fig. 3 bottom).

# Conclusion

An exploration of the vanadium loading process using incipient wetness impregnation with a complexing agent for preparing oxidative propane dehydrogenation catalysts has been undertaken. The primary objective of this approach was to achieve dispersed VO<sub>x</sub> species in a sub-monolayer manner on various catalyst supports with changing pore sizes (and AI content) and make a comprehensive assessment on how the catalytic properties are affected. The oxalic route depends on a complex interplay of many factors. For example in solution, oxalic acid is responsible for dissolution (of the polymeric vanadate), complexation and reduction of V-species. The results revealed that the specific CHA zeolite (Si/AI 30) used here, with the smallest pore size in the study, exhibited the most significant reduction in its surface area (after IWI and calcination) compared to other larger pore (mostly microporous) catalysts. We attributed this to the lesser accessibility for the V-oxalic complexes during the metal deposition via IWI. Furthermore, the analysis of H<sub>2</sub>-TPR suggested a reduced vanadium dispersion within this zeolite. This finding indicates that there might be mass transfer limitations during the catalyst preparation process, *i.e.* limitations for a large oxalic complex to enter the 0.38 nm sized pores. In general, it is likely that a complex mixture of monomeric, dimeric, and polymeric VOx species (but sub-monolayer coverage) is obtained for most other catalysts: their reduction behavior is quite uniform in terms of peak temperature in H<sub>2</sub>-TPD, but the H<sub>2</sub>/V ratios differ substantially. This occurs despite the use of a well-dispersed (and reduced (V->IV) solution of vanadium and large pores. A possible elephant in the room is off course the high temperature calcination following the IWI procedure, which can definitely change or stimulate the V-dispersion and agglomeration as well as V-support interactions heavily.

Interesting catalytic behavior was found for our series of 6 catalysts, as they were subjected to a protocol involving both PDH and OPDH and two pressures. To analyze the product profiles on stream, we introduced an original statistical tool (box-and-whisker) to visualize the decreasing catalytic rates (of production and consumption) with time of different species in one plot. On top, we defined descriptors based on normalized differences when changing conditions from PDH to OPHD and from low to high pressure. These tools allow for a fast quantitative appreciation of catalyst performance relative to each other, as well as to their changing behavior in response to different conditions.

While the MCM-41 structure in general exhibited higher activity, likely linked to its extensive surface area, structures with a more significant population of smaller micropores were found to be more responsive to the transition from PDH to OPDH reaction conditions (adding CO<sub>2</sub>). This behavior could be related to the higher CO<sub>2</sub> adsorption at elevated temperatures (witnessed in TPD) in these materials. BEA zeolites on average where the least performing, likely linked to their strong (and in case of BEA-20 numerous) Alderived acid sites that are not fully neutralized with VOx species. These BEA catalysts lead to cracking and coking side reactions, witnessed both in the box-and-whisker plots and the post-reaction coke analysis. Fewer coke was found for both the largest and smallest pore materials.

Our outlook is that one should try to develop IWI methods to tune the number of oxalic acid V-complexing ligands (1 or 2) to adapt it to the pore size of the support. This could help to strike the right balance between *i*) driving toward mono-atomic highly dispersed V complexes in the IWI solution (oxalic stimulates the dissolution of the polymeric V-oxide precursor); and *ii*) the size of the complex which may cause mass transfer limitations going into certain pores (e.g. in case of 2 ligands and sub-0.4 nm pores).

In summary, this work provides new insights into the vanadium impregnation process in microporous materials and its influence on catalytic OPDH properties. The latter is relevant, as systematic studies on V/porous supports for propane: $CO_2$  mixtures with the aim of co-converting  $CO_2$  are absent thus far. It appears that microporous supports could have benefits, but the impregnation or V-loading procedures should be adapted to the smaller pores.

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## Note

Our presentation in the PREPA13 conference dealt with the same IWI method using oxalic acid but its main focus was the CHA-zeolite including variations of loading and different types of home-made CHA-materials. The reactions studied were the same. Here the focus is put on the IWI and support interactions and a range of supports.

### References

- (1) Carrero, C. A.; Schloegl, R.; Wachs, I. E.; Schomaecker, R. Critical Literature Review of the Kinetics for the Oxidative Dehydrogenation of Propane over Well-Defined Supported Vanadium Oxide Catalysts. ACS Catal. 2014, 4 (10), 3357–3380. https://doi.org/10.1021/cs5003417.
- (2) Monai, M.; Gambino, M.; Wannakao, S.; Weckhuysen, B. M. Propane to Olefins Tandem Catalysis: A Selective Route towards Light Olefins Production. *Chem. Soc. Rev.* 2021, *50* (20), 11503–11529. https://doi.org/10.1039/d1cs00357g.
- (3) Chen, S.; Chang, X.; Sun, G.; Zhang, T.; Xu, Y.; Wang, Y.; Pei, C.; Gong, J. Propane Dehydrogenation: Catalyst Development, New Chemistry, and Emerging Technologies. *Chem. Soc. Rev.* **2021**, *50* (5), 3315–3354. https://doi.org/10.1039/d0cs00814a.
- (4) Akah, A.; Williams, J.; Ghrami, M. An Overview of Light Olefins Production via Steam Enhanced Catalytic Cracking. Catal. Surv. from Asia 2019, 23 (4), 265–276. https://doi.org/10.1007/s10563-019-09280-6.
- (5) Rigamonti; Shah; Gambu; Saeys; Dusselier. Reshaping the Role of CO2 in Propane Dehydrogenation, from Waste Gas to Platform Chemical. ACS Catal. 2022, 9339–9358. https://doi.org/10.1021/acscatal.2c01374.
- (6) Carter, J. H.; Bere, T.; Pitchers, J. R.; Hewes, D. G.; Vandegehuchte, B. D.; Kiely, C. J.; Taylor, S. H.; Hutchings, G. J. Direct and Oxidative Dehydrogenation of Propane: From Catalyst Design to Industrial Application. *Green Chem.* 2021, 23 (24), 9747–9799. https://doi.org/10.1039/d1gc03700e.
- (7) Jiang, X.; Sharma, L.; Fung, V.; Park, S. J.; Jones, C. W.; Sumpter, B. G.; Baltrusaitis, J.; Wu, Z. Oxidative Dehydrogenation of Propane to Propylene with Soft Oxidants via Heterogeneous Catalysis. ACS Catal. 2021, 11 (4), 2182–2234. https://doi.org/10.1021/acscatal.0c03999.
- (8) Nawaz, Z. Light Alkane Dehydrogenation to Light Olefin Technologies: A Comprehensive Review. Rev. Chem. Eng. 2015, 31 (5), 413–436. https://doi.org/10.1515/revce-2015-0012.
- (9) Xing, F.; Ma, J.; Shimizu, K. ichi; Furukawa, S. High-Entropy Intermetallics on Ceria as Efficient Catalysts for the Oxidative Dehydrogenation of Propane Using CO2. *Nat. Commun.* **2022**, *13* (1), 1–10. https://doi.org/10.1038/s41467-022-32842-8.
- (10) Gomez, E.; Kattel, S.; Yan, B.; Yao, S.; Liu, P.; Chen, J. G. Combining CO2 Reduction with Propane Oxidative Dehydrogenation over Bimetallic Catalysts. *Nat. Commun.* 2018, 9 (1), 1–6. https://doi.org/10.1038/s41467-018-03793-w.
- (11) Gambo, Y.; Adamu, S.; Abdulrasheed, A. A.; Lucky, R. A.; Ba-Shammakh, M. S.; Hossain, M. M. Catalyst Design and Tuning for Oxidative Dehydrogenation of Propane – A Review. Appl. Catal. A Gen. 2021, 609 (November 2020), 117914. https://doi.org/10.1016/j.apcata.2020.117914.
- (12) Rigamonti, M. G.; Shah, M.; Gambu, T. G.; Saeys, M.; Dusselier, M. Reshaping the Role of CO2in Propane Dehydrogenation: From Waste Gas to Platform Chemical. ACS Catal. 2022, 12 (15), 9339–9358. https://doi.org/10.1021/acscatal.2c01374.
- (13) Wang, Z. Y.; He, Z. H.; Li, L. Y.; Yang, S. Y.; He, M. X.; Sun, Y. C.; Wang, K.; Chen, J. G.; Liu, Z. T. Research Progress of CO2 Oxidative Dehydrogenation of Propane to Propylene over Cr-Free Metal Catalysts. *Rare Met.* **2022**. https://doi.org/10.1007/s12598-021-01959-y.
- (14) James, O. O.; Mandal, S.; Alele, N.; Chowdhury, B.; Maity, S. Lower Alkanes Dehydrogenation: Strategies and Reaction Routes to Corresponding Alkenes. *Fuel Process. Technol.* **2016**, *149*, 239–255. https://doi.org/10.1016/j.fuproc.2016.04.016.
- (15) Rozanska, X.; Kondratenko, E. V.; Sauer, J. Oxidative Dehydrogenation of Propane: Differences between N2O and O2 in the Reoxidation of Reduced Vanadia Sites and Consequences for Selectivity. *J. Catal.* **2008**, *256* (1), 84–94. https://doi.org/10.1016/j.jcat.2008.03.002.
- (16) Sandupatla, A. S.; Nayak, S. C.; Sivananda, C.; Deo, G. DFT Investigation into the Experimentally Observed Influence of Oxide Support in the ODH of Propane over Supported Vanadia Catalysts. *Catal. Today* **2019**, *325* (May 2018), 18–24. https://doi.org/10.1016/j.cattod.2018.05.058.
- (17) Puigdollers, A. R.; Schlexer, P.; Tosoni, S.; Pacchioni, G. Increasing Oxide Reducibility: The Role of Metal/Oxide Interfaces in the Formation of Oxygen Vacancies. ACS Catal. 2017, 7 (10), 6493–6513. https://doi.org/10.1021/acscatal.7b01913.
- (18) Wachs, I. E. Catalysis Science of Supported Vanadium Oxide Catalysts. Dalt. Trans. 2013, 42 (33), 11762–11769. https://doi.org/10.1039/c3dt50692d.
- (19) Pinna, F. Supported Metal Catalysts Preparation. Catal. Today 1998, 41 (1–3), 129–137. https://doi.org/10.1016/S0920-5861(98)00043-1.
- (20) Munnik, P.; De Jongh, P. E.; De Jong, K. P. Recent Developments in the Synthesis of Supported Catalysts. *Chem. Rev.* 2015, *115* (14), 6687–6718. https://doi.org/10.1021/cr500486u.
- Weckhuysen, B. M.; Keller, D. E. Chemistry, Spectroscopy and the Role of Supported Vanadium Oxides in Heterogeneous Catalysis. *Catal. Today* 2003, 78 (1–4), 25–46. https://doi.org/10.1016/S0920-5861(02)00323-1.
- (22) Chalupka, K.; Thomas, C.; Millot, Y.; Averseng, F.; Dzwigaj, S. Mononuclear Pseudo-Tetrahedral v Species of VSiBEA Zeolite as the Active Sites of the Selective Oxidative Dehydrogenation of Propane. J. Catal. 2013, 305, 46–55. https://doi.org/10.1016/j.jcat.2013.04.020.
- Kosmulski, M. PH-Dependent Surface Charging and Points of Zero Charge. IV. Update and New Approach. J. Colloid Interface Sci. 2009, 337 (2), 439–448. https://doi.org/10.1016/j.jcis.2009.04.072.
- (24) Sushchenko, E.; Kharlamova, T. Textural Characteristics and Structural Peculiarities of Supported Vanadium Oxide Materials Prepared by the NH4VO3 Aqueous Solution Wetness Impregnation. *Key Eng. Mater.* **2015**, *670*, 101–106. https://doi.org/10.4028/www.scientific.net/KEM.670.101.
- (25) Devos, J.; Robijns, S.; Van Goethem, C.; Khalil, I.; Dusselier, M. Interzeolite Conversion and the Role of Aluminum: Toward Generic Principles of Acid

Site Genesis and Distributions in ZSM-5 and SSZ-13. Chem. Mater. 2021, 33 (7), 2516–2531. https://doi.org/10.1021/acs.chemmater.0c04832.

- (26) Devos, J.; Bols, M. L.; Plessers, D.; Goethem, C. Van; Seo, J. W.; Hwang, S. J.; Sels, B. F.; Dusselier, M. Synthesis–Structure–Activity Relations in Fe-CHA for C–H Activation: Control of Al Distribution by Interzeolite Conversion. *Chem. Mater.* 2020, 32 (1), 273–285. https://doi.org/10.1021/acs.chemmater.9b03738.
- (27) Devos, J.; Shah, M. A.; Dusselier, M. On the Key Role of Aluminium and Other Heteroatoms during Interzeolite Conversion Synthesis. RSC Advances. The Royal Society of Chemistry July 2021, pp 26188–26210. https://doi.org/10.1039/d1ra02887a.
- (28) Li, Y.; Yu, X.; Zhang, Q.; Kondratenko, V. A.; Wang, Y.; Cui, G.; Zhou, M.; Xu, C.; Kondratenko, E. V.; Jiang, G. The Nature of VOx Structures in HMS Supported Vanadium Catalysts for Non-Oxidative Propane Dehydrogenation. J. Catal. 2022, 413, 658–667. https://doi.org/10.1016/j.jcat.2022.07.017.
- (29) Grant, J. T.; Carrero, C. A.; Love, A. M.; Verel, R.; Hermans, I. Enhanced Two-Dimensional Dispersion of Group v Metal Oxides on Silica. ACS Catal. 2015, 5 (10), 5787–5793. https://doi.org/10.1021/acscatal.5b01679.
- (30) Kondratenko, E. V.; Cherian, M.; Baerns, M. Oxidative Dehydrogenation of Propane over Differently Structured Vanadia-Based Catalysts in the Presence of O2 and N2O. Catal. Today 2006, 112 (1–4), 60–63. https://doi.org/10.1016/j.cattod.2005.11.028.
- (31) Muhammad, I.; Makwashi, N.; Manos, G. Catalytic Degradation of Linear Low-Density Polyethylene over HY-Zeolite via Pre-Degradation Method. J. Anal. Appl. Pyrolysis 2019, 138 (September 2018), 10–21. https://doi.org/10.1016/j.jaap.2018.11.025.
- (32) Bond, G.; Tahir, F. Vanadium Oxide Monolayer Catalysts. Appl. Catal. 1991, 111 (2), 215–224. https://doi.org/10.1524/zpch.1978.111.2.215.
- (33) Shan, Y. L.; Sun, H. L.; Zhao, S. L.; Tang, P. L.; Zhao, W. T.; Ding, J. W.; Yu, W. L.; Li, L. N.; Feng, X.; Chen, D. Effects of Support and CO2on the Performances of Vanadium Oxide-Based Catalysts in Propane Dehydrogenation. ACS Catal. 2022, 5736–5749. https://doi.org/10.1021/acscatal.2c00878.
- (34) Xiong, C.; Chen, S.; Yang, P.; Zha, S.; Zhao, Z. J.; Gong, J. Structure-Performance Relationships for Propane Dehydrogenation over Aluminum Supported Vanadium Oxide. ACS Catal. 2019, 9 (7), 5816–5827. https://doi.org/10.1021/acscatal.8b04701.
- (35) Costa Pessoa, J. Thirty Years through Vanadium Chemistry. J. Inorg. Biochem. 2015, 147, 4–24. https://doi.org/10.1016/j.jinorgbio.2015.03.004.
- (36) Bruyère, V. I. E.; Garcia Rodenas, L. A.; Morando, P. J.; Blesa, M. A. Reduction of Vanadium(V) by Oxalic Acid in Aqueous Acid Solutions. J. Chem. Soc. Dalt. Trans. 2001, No. 24, 3593–3597. https://doi.org/10.1039/b103320b.
- (37) Lasalle, M. J.; Cobble, J. W. The Entropy and Structure of the Pervanadyl Ion. J. Phys. Chem. **1955**, 59 (6), 519–524. https://doi.org/10.1021/j150528a010.
- (38) Hernández-Maya, M. S.; Espinosa-Lobo, C. B.; Cabanzo-Hernández, R.; Mejía-Ospino, E.; Baldovino-Medrano, V. G. Effects of PH and Vanadium Concentration during the Impregnation of Na-SiO2 Supported Catalysts for the Oxidation of Propane. *Mol. Catal.* 2022, *520* (February). https://doi.org/10.1016/j.mcat.2022.112158.
- (39) Vanadium and Its Compounds. In Vanadium; Yang, B., He, J., Zhang, G., Guo, J., Eds.; Published by Elsevier Ltd, 2021; pp 9–32. https://doi.org/10.1016/b978-0-12-818898-9.00002-4.
- (40) Love, A. M.; Carrero, C. A.; Chieregato, A.; Grant, J. T.; Conrad, S.; Verel, R.; Hermans, I. Elucidation of Anchoring and Restructuring Steps during Synthesis of Silica-Supported Vanadium Oxide Catalysts. *Chem. Mater.* **2016**, *28* (15), 5495–5504. https://doi.org/10.1021/acs.chemmater.6b02118.
- (41) Thommes, M.; Kaneko, K.; Neimark, A. V.; Olivier, J. P.; Rodriguez-Reinoso, F.; Rouquerol, J.; Sing, K. S. W. Physisorption of Gases, with Special Reference to the Evaluation of Surface Area and Pore Size Distribution (IUPAC Technical Report). *Pure Appl. Chem.* 2015, 87 (9–10), 1051–1069. https://doi.org/10.1515/pac-2014-1117.
- (42) Chen, C.; Sun, M.; Hu, Z.; Liu, Y.; Zhang, S.; Yuan, Z. Y. Nature of Active Phase of VOx Catalysts Supported on SiBeta for Direct Dehydrogenation of Propane to Propylene. *Chinese J. Catal.* **2020**, *41* (2), 276–285. https://doi.org/10.1016/S1872-2067(19)63444-3.