Heterogeneous Catalysis

Origin of the Activity Trend in the Oxidative Dehydrogenation of Ethanol over VO₄/CeO₂**

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Abstract: Supported vanadia (VO₄) is a versatile catalyst for various redox processes where ceria-supported VO₄ have shown to be particularly active in the oxidative dehydrogenation (ODH) of alcohols. In this work, we clarify the origin of the volcano-shaped ethanol ODH activity trend for VO₄/CeO₂ catalysts using operando quick V K- and Ce L₃-edge XAS experiments performed under transient conditions. We quantitatively demonstrate that both vanadium and cerium are synergistically involved in alcohol ODH. The concentration of reversible Ce⁴⁺/Ce³⁺ species was identified as the main descriptor of the alcohol ODH activity. The activity drop in the volcano plot, observed at above ca. 3 V nm⁻² surface loading (ca. 30% of VO₄ monolayer coverage), is related to the formation of spectator V⁴⁺ and Ce³⁺ species, which were identified here for the first time. These results might prove to be helpful for the rational optimization of VO₄/CeO₂ catalysts and the refinement of the theoretical models.

Introduction

Supported vanadia (VO₄) is a well-known catalyst for selective oxidation and reduction processes, including oxidation of sulfur dioxide to sulfur trioxide,[1] selective catalytic reduction of nitrogen oxides with ammonia,[2] oxidative dehydrogenation (ODH) of short alkanes and alcohols to the corresponding alkenes and aldehydes,[3, 4] and oxidation of n-butane to maleic anhydride.[5] The activity of the supported VO₄ catalysts depends on a variety of parameters such as VO₄ surface loading, level of dispersion as well as nature of support.[6, 7] Ceria-supported VO₄ (VO₄/CeO₂) demonstrates outstanding activity in comparison with silica- or alumina-supported VO₄ in oxidative dehydrogenation (ODH) of short alkanes and alcohols.[8, 9] It is generally accepted that ODH of alkanes and alcohols on supported VO₄ catalysts proceeds via a Mars–van Krevelen (MvK) mechanism.[10, 11] The MvK mechanism consists of two main steps: (i) oxidation of a substrate (alkane or alcohol) on the surface of the catalyst accompanied by the formation of an oxygen vacancy and reduction of the metal center/s and (ii) a faster re-oxidation of the catalyst by molecular oxygen.[8, 11, 12]

For the majority of supported VO₄ catalysts, the redox activity of metal centers during ODH is exclusively associated with the redox activity of vanadium. However, in the case of VO₄/CeO₂, it is generally accepted that cerium is more active.[13] This idea was originally proposed in the work of Bañares et al. upon investigating a VO₄/CeO₂ catalyst in ethane ODH[14, 15] where the V K-edge XANES under catalytic conditions demonstrated no reduction of V⁵⁺. At the same time, the authors detected the CeVO₄ phase (containing Ce⁴⁺ and V⁵⁺) in the spent catalyst by Raman spectroscopy, which suggested that cerium can be potentially reducible. Since this first report, the CeVO₄ phase formed during alkane ODH was shown not to be the most active species for ODH.[16, 17] The structure of isolated VO₄ species on CeO₂(111) investigated by density functional theory (DFT)[18–20] showed that vanadium is always stabilized in the highest oxidation state. Moreover, upon oxygen vacancy formation, the electrons are always stabilized on Ce⁴⁺ species. These results were confirmed by DFT studies of methanol ODH on isolated VO₄ species supported on CeO₂.[21, 22] two cerium ions accept two electrons and stabilize vanadium in its highest +5 oxidation state. Later DFT work performed by the same group on trimeric VO₄ species (which are thermodynamically more stable on the CeO₂ support than isolated VO₄)[18–20], however, showed that upon methanol oxidation vanadium can also accept one of two electrons.[23] Experimental evidence of vanadium reduction in VO₄/CeO₂ catalysts was also reported in the literature. Abbott et al.[24] investigated a supported VO₄/CeO₂ catalyst in methanol ODH by photoelectron spectroscopy and observed vanadium reduction upon catalyst exposure to methanol. Ober et al.[25] detected cerium reduction and oxygen vacancy formation in a VO₄/CeO₂ catalyst using...
operando wavelength-selective Raman spectroscopy. UV/Vis experiments, reported in the same work, identified transitions in the d-d region, which might correspond to the formation of Ce$^{3+}$ and V$^{4+/3+}$ species. These transitions, however, were exclusively assigned to the Ce$^{3+}$ species, relying on previous theoretical modeling.[18,21,22,24] Iglesias-Juez et al.[26] detected vanadium reduction using in situ V K-edge XANES on a bilayered supported VO$_2$/CeO$_2$/SiO$_2$ system in ethane ODH. The appearance of V$^{4+}$ was explained by inefficient V$^{5+}$ stabilization by the thin CeO$_2$ layer. Vining et al.[27] investigated bilayered VO$_2$/CeO$_2$/SiO$_2$ catalysts in methanol ODH using V K- and Ce L$_{3}$-edge XAS and detected both vanadium and cerium reduction upon catalyst exposure to methanol. Insufficient time resolution (ca. 5 min), however, did not allow quantifying the rates of V$^{4+}$ and Ce$^{3+}$ formation and the order of their appearance necessary to elucidate their roles in catalysis. Thus, despite a number of investigations, there is no consensus on the active redox species for ODH in VO$_2$/CeO$_2$ systems, which hampers a further rational optimization of this catalyst. In our previous work, we demonstrated that operando quick XAS combined with a transient experimental strategy provides quantitative information on the redox activity of metal centers involved in the Mars–van Krevelen mechanism of carbon monoxide and ethanol oxidation on various catalysts.[26–32] In particular, for the bilayered VO$_2$/TiO$_2$/SiO$_2$ catalyst, we have shown that V$^{5+}$ to V$^{4+}$ reduction upon ethanol oxidation is kinetically coupled with acetaldehyde formation, while the redox activity of titanium was shown to be not directly involved in the catalytic cycle.[32]

In this work, we applied the same transient XAS methodology to uncover the redox processes involved in ethanol ODH on VO$_2$/CeO$_2$ catalysts. We prepared a series of VO$_2$/CeO$_2$ catalysts with different VO$_2$ coverage (1.4–13.6 \text{ V nm}^{-2}) and high dispersion, as confirmed by Raman spectroscopy. By using XAS under transient conditions, we show that the formation of acetaldehyde is kinetically coupled to the simultaneous reduction of cerium and vanadium species, which suggests that they both constitute the active site. Moreover, we demonstrated that the fraction of reversible Ce$^{3+/4+}$ species in VO$_2$/CeO$_2$ catalysts appears to be the main descriptor of the catalytic activity.

Results and Discussion

We used a high surface area CeO$_2$ ($S_{\text{BET}} = 193 \pm 5$ \text{ m}^2\text{g}^{-1}$) synthesized via the glycothermal route[33] as catalyst support. By incipient-wetness impregnation with VO(O-i-C$_3$H$_7$)$_2$, we prepared a series of VO$_2$/CeO$_2$ catalysts with a wide range of VO$_2$ loading (4–20 wt\% \text{ V O}_3) corresponding to a surface density of 1.4–13.6 \text{ V nm}^{-2} (monolayer loading corresponds to ca. 9 \text{ V nm}^{-2})[34,35]. A list of all catalysts and their physical characteristics are shown in Table 1. The numbers in the catalysts’ designations describe the VO$_2$ surface density (V/\text{ nm}^2), calculated using the surface area of the final materials.

Figure 1 shows the activity of all catalysts in ethanol ODH normalized per catalyst weight. Bare CeO$_2$ demonstrates significant activity in ethanol oxidation, which is in agreement with the literature.[33] Deposition of VO$_2$ species on ceria leads to a strong activity increase (up to 6 times). The activity trend versus VO$_2$ loading shows a volcano-shaped profile with a maximum at ca. 3 \text{ V nm}^{-2} (similar trends are also observed at higher temperatures, Figures S1–S2). The strongest activity increase (see the derivative plot in Figure S3) corresponds to the minimal addition of VO$_2$ to bare CeO$_2$. A volcano-shaped activity trend was previously observed for VO$_2$/CeO$_2$ catalysts in propane ODH,[17] where the decrease of the catalyst activity with high VO$_2$ loading was assigned to the formation of the CeVO$_3$ phase. Here we will show that the origin of the volcano-type activity trend is different and related to the synergetic promotion of highly-dispersed VO$_2$ species and CeO$_2$ as VO$_2$ species alone (e.g. when supported silica or alumina) and CeO$_2$ surface alone show much lower ODH activity per vanadium or cerium atom compared to VO$_2$/CeO$_2$ catalysts.

Bare CeO$_2$ demonstrated relatively high selectivity towards acetaldehyde (80–90\%), which further increased with VO$_2$ deposition (93–95\% for 1.4 V/CeO$_2$ and >98\% for the catalysts with higher vanadium loading, Figure S4). The main side product was CO$_2$. Apparently, bare ceria contains sites on which ethanol combustion to CO$_2$ occurs; upon vanadium oxide deposition, VO$_2$ species bind with these sites, which leads to the elimination of full ethanol.

<table>
<thead>
<tr>
<th>Catalyst design:</th>
<th>VO$_2$ loading [wt%]</th>
<th>BET surface area [m$^2$ g$^{-1}$]</th>
<th>VO$_2$ surface density [V nm$^{-2}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeO$_2$</td>
<td>0</td>
<td>193</td>
<td>0</td>
</tr>
<tr>
<td>1.4 V/CeO$_2$</td>
<td>4</td>
<td>184</td>
<td>1.4</td>
</tr>
<tr>
<td>2.1 V/CeO$_2$</td>
<td>6</td>
<td>189</td>
<td>2.1</td>
</tr>
<tr>
<td>3.1 V/CeO$_2$</td>
<td>8</td>
<td>169</td>
<td>3.1</td>
</tr>
<tr>
<td>4.1 V/CeO$_2$</td>
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<td>161</td>
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<td>147</td>
<td>5.9</td>
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<tr>
<td>7.9 V/CeO$_2$</td>
<td>16</td>
<td>134</td>
<td>7.9</td>
</tr>
<tr>
<td>13.6 V/CeO$_2$</td>
<td>20</td>
<td>97</td>
<td>13.6</td>
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</tbody>
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Figure 1. Activity (left axis) and selectivity (right axis) trends of the VO$_2$/CeO$_2$ catalysts in ethanol ODH at 160 °C normalized per catalyst weight (1.6 vol. % \text{ EtOH}, 6.4 vol. % \text{ O$_2$ in He, total flow 50 mL min}^{-1}, ethanol conversion < 20\%).
combustion and an increase of selectivity to acetaldehyde. For acetaldehyde formation, all catalysts demonstrated near zero order in ethanol and oxygen (Figures S5, S6). To test whether the activity trend of VO/CeO$_2$ catalysts could be related to the state of VO$_3$ species on the surface (e.g. isolated or oligomeric species) or to the formation of additional phases (e.g. CeVO$_4$, V$_2$O$_5$), we first analyzed the catalysts using ex situ X-ray diffraction (XRD) and in situ Raman spectroscopy.

Ex situ XRD demonstrated the presence of only the nanocrystalline CeO$_2$ phase in the samples up to 16 wt % V$_2$O$_5$ loading (7.9 V/CeO$_2$) (details and Figures are in Supporting Information, Section 4.1). Raman spectroscopy is a powerful method for the chemical speciation of supported VO$_3$ which can potentially distinguish the structure of different VO$_3$ oligomers and detect minor quantities of crystalline phases, such as V$_2$O$_5$ and CeVO$_4$ nanoparticles. In situ Raman spectroscopy measured under dry conditions (10 vol. % O$_2$ in Ar, 250°C, details, and Figures are in Supporting Information, Section 4.1) revealed, that in all investigated VO/CeO$_2$ catalysts, VO$_3$ species are present as a mixture of different oligomers (dimers, trimers, and polymers), whereby almost no monomeric isolated VO$_3$ species were detected. This agrees with previous findings, reporting that monomeric VO$_3$ species on the CeO$_2$ surface are the least stable and prone to oligomerize upon heating.[14,36,37] In addition, for all samples except 13.6 V/CeO$_2$, no crystalline V$_2$O$_5$ was detected, which also agrees with the literature suggesting that 9–9.2 V nm$^{-2}$ is the maximal loading of VO$_3$ species on CeO$_2$ before crystalline V$_2$O$_5$ is formed.[14,34] No bands associated with the CeVO$_4$ phase were detected either in the as-prepared catalysts or in the catalysts used in ethanol ODH (Figure S26). Thus, Raman spectroscopy, which gives insight into the VO$_3$ speciation, could not explain the origin of the volcano-shaped activity trend for VO/CeO$_2$ catalysts (Figure 1). In particular, the maximum of the ethanol ODH activity observed for ca. 3 V nm$^{-2}$ loading could not be correlated to the presence of a specific VO$_3$ oligomer or other vanadium-containing phases.

To access the redox properties of vanadium and cerium during ethanol ODH, we used operando quick XAS under steady-state conditions. Very similar trends for the measurable Ce$^{4+}$ and Ce$^{3+}$ fractions increase and within 5 min of ethanol exposure reach a certain level in the 5 min time span (referred to as “maximal” V$^{4+}$ and Ce$^{3+}$ species (Figure 2b)). Upon switching off the oxygen supply, the V$^{4+}$ and Ce$^{3+}$ fractions increase and within 5 min of ethanol exposure reach a certain level in the 5 min time span (referred to as “maximal” V$^{4+}$ and Ce$^{3+}$ species (Figure 2b)). The concentration of the reversible Ce$^{4+}$ and Ce$^{3+}$ species decreases as a function of temperature and VO$_3$ density. For the 1.4 V/CeO$_2$ catalyst (Figure 2b), the concentration of the reversible Ce$^{4+}$ species is higher than the concentration of the reversible V$^{4+}$ species. With the increase of the VO$_3$ surface density, the fraction of the reversible Ce$^{4+}$ species progressively increases and for the 5.9 V/CeO$_2$ catalysts, this fraction exceeds the fraction of the reversible Ce$^{4+}$ species (Figure 2c–e).

To verify whether the formation of V$^{4+}$ and Ce$^{3+}$ species is present simultaneously or consecutively, we normalized the observed concentration profiles to unity. Figure 2f shows the results for the 7.9 V/CeO$_2$ catalyst at 170°C. The coevolution of V$^{4+}$ and Ce$^{3+}$, evident from the normalized concentration profiles, suggests that V$^{4+}$ and Ce$^{3+}$ species are formed simultaneously, within the achieved temporal resolution (2 s). In contrast, the V$^{4+}$ species (detected only in the 7.9 V/CeO$_2$ catalyst) appears with a slight delay and evolves slower (Figure 2f), suggesting that V$^{4+}$ formation is a secondary process (probably appearing upon deeper V$^{4+}$ reduction) and therefore is most likely not taking place under steady-state conditions. Very similar trends for the V$^{4+}$ and Ce$^{3+}$ concentration profiles, observed for all catalysts at all temperatures (Figure S11), suggest that the active sites for ethanol ODH contain both vanadium and cerium changing their oxidation states in concert. This finding does not fully agree with the majority of previously reported DFT calculations, which suggested that vanadium remains in the V$^{5+}$ state.[10,21] These calculations, however, were mainly performed with isolated VO$_3$ species, which are the least thermodynamically stable[18,20] and are predominantly not present in our catalysts. In contrast, DFT models for trimeric VO$_3$ species suggested that upon methanol
ODH, one electron should be accepted by vanadium and the other one by cerium, which partially agrees with our observations. VO oligomers with greater size, to the best of our knowledge, were not investigated by DFT.

During oxygen cut-off experiments, no other product was detected apart from acetaldehyde (Figure S12), indicating that the mechanism of ethanol oxidation does not change in the absence of molecular oxygen. The ethanol ODH MvK mechanism involves the transfer of two electrons, according to Equations (1) and (2):

\[
\begin{align*}
\text{C}_2\text{H}_5\text{OH} + \text{O}^{2-} + 2\text{V}^{5+} = \\
\text{CH}_3\text{CHO} + \text{H}_2\text{O} + 2\text{V}^{4+} + [-\cdot\cdot\cdot]\_0
\end{align*}
\]

\[
\begin{align*}
\text{C}_2\text{H}_5\text{OH} + \text{O}^{2-} + 2\text{Ce}^{4+} = \\
\text{CH}_3\text{CHO} + \text{H}_2\text{O} + 2\text{Ce}^{3+} + [-\cdot\cdot\cdot]\_0.
\end{align*}
\]

where \([-\cdot\cdot\cdot]\_0\) is an oxygen vacancy.

Thus, the sum of the initial rates of vanadium and cerium reduction in ethanol should be two times higher than the rate of steady-state acetaldehyde production. We quantified the rates of \(\text{V}^{4+}\) and \(\text{Ce}^{3+}\) formation by fitting the \(\text{V}^{4+}\) and \(\text{Ce}^{3+}\) concentration profiles in each experiment with an exponential decay function and taking a derivative at the time when the oxygen feed was switched off (see details in Supporting Information, Section 3.7). Figures 3a–e compare for each catalyst the initial \(\text{V}^{4+}\) and \(\text{Ce}^{3+}\) formation rates in the absence of oxygen and their sum with the acetaldehyde formation rates measured at several temperatures. For all catalysts, the ratio between the rates does not depend significantly on the temperature. For the catalyst with the lowest VO loading (1.4 V/CeO\(_2\)), the rate of \(\text{Ce}^{3+}\) formation is higher than the rate of \(\text{V}^{4+}\) formation (Figure 3 b). With an increase in VO loading (Figures 3c–e), the \(\text{V}^{4+}\) formation rate progressively increases and surpasses that of the \(\text{Ce}^{3+}\) formation. The sum of the \(\text{V}^{4+}\) and \(\text{Ce}^{3+}\) formation rates is on average 1.6–3.2 times higher than the corresponding acetaldehyde production rates (Tables S1–S5), which roughly matches the electron balance of the MvK mechanism. The imperfect matching to the electron balance is likely related to the propagation of experimental errors at every stage of the multi-stage data analysis procedure (noise of the XAS data, MCR analysis, Ce L\(_3\) edge self-absorption correction, fitting with exponential decay function, etc.).

To evaluate the involvement of vanadium and cerium in the MvK cycle of ethanol ODH in each catalyst, we plotted the correlation between the concentrations of reversible \(\text{V}^{4+}\) and \(\text{Ce}^{3+/4+}\) species (taken from Figures 2a–e) in Figure 3 f. All points for each catalyst (corresponding to different temperatures) can be fitted with a linear function with a slope \(n\), which represents the number of electrons transferred to cerium per electron transferred to vanadium. The slope \(n\) progressively decreases from 2.4 for 1.4 V/CeO\(_2\) to 0.4 for 7.9 V/CeO\(_2\). These results further indicate that the redox reaction in each catalyst during the oxygen cut-off experiment at 170°C.

Figure 2. \(\text{Ce}^{3+}, \text{V}^{4+}\), and \(\text{V}^{5+}\) concentration profiles during oxygen cut-off experiments at 170°C for a) pure CeO\(_2\) and supported VO/\(\text{CeO}_2\) catalysts containing b) 1.4, c) 3.1, d) 5.9, e) 7.9 V nm\(^{-2}\). The corresponding catalytic activity changes in a similar manner as in Figure 1 and is shown in Figure S1. f) The normalized changes of the \(\text{V}^{4+}\), \(\text{V}^{5+}\), and \(\text{Ce}^{3+}\) concentrations in the 7.9 V/CeO\(_2\) catalyst during the oxygen cut-off experiment at 170°C.

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much faster than the reduction step, oxidation step in the MvK cycle of alcohol ODH should be and Figures S7–10). According to the literature, the re-experiments. The quantity of these species can be rather stable in the presence of oxygen during oxygen cut-off experiments. The majority of the observed reduced steady-state species must be spectators. The V\textsuperscript{3+} and Ce\textsuperscript{4+} species are rather stable and most likely do not origin of the steady-state V\textsuperscript{4+} and Ce\textsuperscript{4+} species, which are stable in the presence of oxygen during oxygen cut-off experiments. The quantity of these species can be rather large, with up to 30% of cations on the surface (Figure 2 and Figures S7–10). According to the literature, the re-oxidation step in the MvK cycle of alcohol ODH should be much faster than the reduction step,	extsuperscript{[9]} thus, theoretically the concentration of the reduced V\textsuperscript{4+} and Ce\textsuperscript{4+} species observed under steady-state conditions should be negligible. To verify whether the re-oxidation is significantly faster, we quantified the initial rates of Ce\textsuperscript{4+} re-oxidation upon oxygen introduction in oxygen cut-off experiments (for details refer to Supporting Information, Section 3.8). The results (Tables S6, S7) suggest that the rate of Ce\textsuperscript{4+} re-oxidation in 5.9 V/CeO\textsubscript{2} and 7.9 V/CeO\textsubscript{2} catalysts is 25–60 times faster than Ce\textsuperscript{4+} reduction. For the catalysts with the lower VO\textsubscript{2} surface density, the re-oxidation rates of Ce\textsuperscript{4+} were even faster and could not be reasonably estimated since the catalyst re-oxidation rate is comparable to the gas exchange in the cell (95% in 2.4 s). Thus, only a very small concentration of active Ce\textsuperscript{3+} species (< 4%, Tables S6, S7) should be present under steady-state ethanol ODH conditions, suggesting that the majority of the observed reduced steady-state species must be spectators. The V\textsuperscript{4+} re-oxidation rates could not be reasonably quantified due to the lower spectral quality of V K-edge XAS data and consequently insufficient temporal resolution (2 s) for the quantitative analysis.

To investigate the formation and stability of the steady-state V\textsuperscript{4+} and Ce\textsuperscript{4+} species, we performed additional experiments. After standard pre-treatment in oxygen at 400 °C, the catalysts do not contain any traces of V\textsuperscript{3+} or Ce\textsuperscript{3+} species (Figure S14). The steady-state Ce\textsuperscript{3+} and V\textsuperscript{4+} species appear almost instantly as soon as ethanol is introduced to the feed (3 vol. % EtOH, 12 vol. % O\textsubscript{2} in He), however, the formation of the steady-state V\textsuperscript{4+} in the 5.9 V/CeO\textsubscript{2} catalyst is delayed by ca. 4 s to the Ce\textsuperscript{3+} formation. The ethanol cut-off experiments (EtOH + O\textsubscript{2} versus O\textsubscript{2} switching) performed with the 1.4 V/CeO\textsubscript{2} catalyst at 140 and 180 °C (Figure S15) showed that the concentrations of the steady-state V\textsuperscript{4+} and Ce\textsuperscript{3+} only slightly decreased in oxygen feed and is quickly restored to the initial values as soon as ethanol is reintroduced. These results indicate that the steady-state Ce\textsuperscript{3+} and V\textsuperscript{4+} species are rather stable and most likely do not participate in the ethanol ODH catalytic cycle. It was previously reported in the literature that a CeVO\textsubscript{4} phase (consisting of Ce\textsuperscript{3+} and V\textsuperscript{4+}) could be formed at high temperatures (> 450 °C) in the alkane ODH reactions and can potentially be a spectator phase.\textsuperscript{[14–16]} We measured in situ Raman spectra of the used catalysts (tested in the oxygen cut-off experiments) and observed no bands corresponding to CeVO\textsubscript{4} (786, 799, and 860 cm\textsuperscript{-1}) (Figure S26). The same was suggested by XRD (Figure S24). This agrees with the in situ Raman spectroscopy results reported by
Ober et al.,\textsuperscript{[25]} where the authors studied in situ ethanol ODH and detected no evidence of CeVO\textsubscript{2} formation. Finally, subsequent treatment in oxygen at 400°C resulted in the complete oxidization of all species indicating that the formation of the steady-state reduced species is fully reversible (Figure S16–S18).

When analyzing the concentrations of the steady-state species, we have found a surprising correlation. In Figure 4, we plot the steady-state Ce\textsuperscript{3+} concentration versus the steady-state V\textsuperscript{4+} concentration observed during cut-off experiments for all catalysts and all temperatures. The content of the steady-state Ce\textsuperscript{3+} and V\textsuperscript{4+} strongly depends on the VO\textsubscript{x} loading and only slightly on the temperature and the time on stream (details in Figure S19). The correlation shows a linear trend with a slope close to one, suggesting that the steady-state concentration of V\textsuperscript{4+} and Ce\textsuperscript{3+} species are linked to or stabilized in the vicinity of each other.

Figure 5 summarizes the concentrations of maximal V\textsuperscript{4+} and Ce\textsuperscript{3+} (formed within 5 min in oxygen-free phase), steady-state V\textsuperscript{4+} and Ce\textsuperscript{3+} and reversible V\textsuperscript{5+}/V\textsuperscript{4+} and Ce\textsuperscript{4+}/Ce\textsuperscript{3+}, quantified from the transient XAS experiments (example shown in Figure 2b), for a series of catalysts with progressively increasing VO\textsubscript{x} density. All the presented data correspond to 170°C. Important to note is that the fraction of the reversible V\textsuperscript{5+}/V\textsuperscript{4+} and Ce\textsuperscript{4+}/Ce\textsuperscript{3+} species observed in oxygen cut-off experiments may not represent the total amount of the redox-active species in a catalyst but can still be used to correlate the redox and catalytic properties of the catalysts.

In the case of vanadium, the concentrations of the maximally V\textsuperscript{4+}, the reversible V\textsuperscript{5+}/V\textsuperscript{4+}, and the steady-state V\textsuperscript{4+} species steadily grow with VO\textsubscript{x} density (Figure 5a). Moreover, if these values are normalized to the total amount of vanadium, they become almost constant (Figure S20). This suggests that the redox properties of vanadium are independent of the VO\textsubscript{x} surface loading and cannot explain the volcano-shaped activity trend (Figure 1a).

For cerium, the situation is different. In Figure 5b, the concentration of the maximal Ce\textsuperscript{3+} increases with vanadium surface loading up to 3.1 V nm\textsuperscript{-2}, which reflects the promotion of cerium reducibility upon deposition of VO\textsubscript{x} species. Maximal Ce\textsuperscript{3+} species slightly drop after 3.1 V nm\textsuperscript{-2} mainly due to the decrease in the total number of cerium species in the catalysts (a similar trend is observed for the data normalized to the cerium content, Figure S20). In contrast, the concentration of the steady-state Ce\textsuperscript{3+} (spectator species) steadily increases with VO\textsubscript{x} loading. As a consequence, the concentration of the reversible Ce\textsuperscript{4+}/Ce\textsuperscript{3+} (true redox participating/active species, Figure 5b, blue plot) has a volcano-shape profile with a maximum obtained at a vanadium surface loading of 3.1 V nm\textsuperscript{-2}. This profile closely resembles the catalysts’ activity trend (Figure 5b, red plot).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4.png}
\caption{The amount of the steady-state Ce\textsuperscript{3+} versus the amount of the steady-state V\textsuperscript{4+} in the ethanol-oxygen feed (3 vol. % EtOH, 12 vol. % O\textsubscript{2} in He). The different dots marked with one color represent the same catalyst measured in different experiments; more details are in Figure S19.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5.png}
\caption{The concentrations of maximally reduced, steady-state reduced, and reversible vanadium (a) and cerium (b) species in the VO\textsubscript{x}/CeO\textsubscript{2} catalysts detected in oxygen cut-off experiments at 170°C (derived from Figure 2). Figure b also includes the catalysts’ activity trend (right axis).}
\end{figure}
Thus, the concentration of the reversible Ce$^{4+}/Ce^{3+}$ is proposed to be the main descriptor of the catalytic activity of VO$_x$/CeO$_2$ catalysts.

In Figure 6, we suggest a geometrical model of the VO$_x$/CeO$_2$ surface with different VO$_x$ densities, depicting the hypothetical location of the active (reversible) V$^{4+}$/V$^{4+}$ and Ce$^{4+}$/Ce$^{3+}$ and the spectator (steady-state) V$^{4+}$ and Ce$^{3+}$ species, and its correlation with the ethanol ODH activity. The location of these species is hypothetical because we cannot distinguish by XAS the structures of vanadium and cerium species with the same oxidation state (e.g. V$^{4+}$ or Ce$^{4+}$), which form reversible and steady-state sites.

This model is based on the surface structures observed by Baron et al. from their high-resolution scanning tunneling microscopy studies of a CeO$_2$ (111) surface covered with VO$_x$ species. The authors reported that each vanadium atom is located between three cerium atoms and the vanadyl oxygen is pointing up, perpendicular to the surface. In addition, it was shown that in the VO$_x$/CeO$_2$ catalyst with a VO$_x$ surface density lower than 4.3 V nm$^{-2}$, VO$_x$ species are mainly present in the form of trimers; whereas in the catalysts with a surface density higher than 4.3 V nm$^{-2}$, the CeO$_2$ surface is mainly populated by VO$_x$ hexamers and ill-defined mainly two-dimensional agglomerates (which also agrees with our Raman observations (Figure S26)).

Both cerium and vanadium contribute to the ODH activity of the VO$_x$/CeO$_2$ catalysts. The addition of VO$_x$ species on the CeO$_2$ surface promotes the redox activity of cerium (Ce$^{4+}$ species become easier reducible). The volcano-shaped ethanol ODH activity trend as a function of VO$_x$ surface density mainly correlates to the quantity of the reversible Ce$^{4+}$/Ce$^{3+}$ species (light green atoms in Figure 6), which is one of the main descriptors of the catalytic activity. The 3.1 V nm$^{-2}$ coverage is optimal because at this surface density vanadium maximally promotes the reducibility of cerium; a further increase of the VO$_x$ coverage just stabilizes the Ce$^{3+}$ spectators.

**Conclusion**

We prepared a series of the high surface area supported VO$_x$/CeO$_2$ catalysts with a vanadium surface density of 0–7.9 V nm$^{-2}$, containing only highly dispersed VO$_x$ species and no additional crystalline phases. The catalytic tests in ethanol ODH showed that the activity of the supported VO$_x$/CeO$_2$ catalysts (normalized on catalyst weight) has a volcano-shaped trend with a maximum at ca. 3 V nm$^{-2}$. Raman spectroscopy demonstrated that VO$_x$ species are present in multiple oligomeric forms with a slightly increased level of polymerization upon the increase of loading, which, however, does not easily explain the ODH activity trend.Transient operando XAS experiments allowed distinguishing different types of vanadium and cerium surface species: (i) the steady-state V$^{4+}$ and Ce$^{3+}$ species appear under catalytic conditions but do not participate in the catalytic cycle; (ii) the reversible V$^{4+}$ and Ce$^{4+}$ species mediate the formation of acetaldehyde according to the MvK mechanism synergistically enhancing the activity of each other. The catalytic activity correlates with the fraction of the reversible Ce$^{4+}/Ce^{3+}$ species, which is determined by the VO$_x$ surface density. The deposition of VO$_x$ species on CeO$_2$ promotes the reducibility of CeO$_2$ and is responsible for the
appearance of the majority of the reversible Ce\textsuperscript{4+/3+} species but, at the same time, also leads to the stabilization of the inactive steady-state V\textsuperscript{4+} and Ce\textsuperscript{3+} species. These results provide the basis for the rational optimization of VO\textsubscript{3}/CeO\textsubscript{2} catalysts for ODH of alcohols as well as the refinement of mechanistic models of supported VO, catalysts and ceria-based materials.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Origin of the Activity Trend in the Oxidative Dehydrogenation of Ethanol over VOₓ/CeO₂

Using operando time-resolved X-ray absorption spectroscopy, we investigated the origin of the volcano-shaped activity trend in the oxidative dehydrogenation of ethanol over VOₓ/CeO₂ catalysts as a function of VOₓ surface coverage. Vanadium and cerium synergistically change their oxidation states during the catalytic cycle. The catalytic activity correlates with the concentration of reversible Ce⁴⁺/³⁺ species.