Molecular-Level Understanding of CeO₂ as a Catalyst for Partial Alkyne Hydrogenation

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Supporting Information

ABSTRACT: The unique catalytic properties of ceria for the partial hydrogenation of alkenes are examined for acetylene hydrogenation. Catalytic tests over polycrystalline CeO₂ at different temperatures and H₂/C₂H₂ ratios reveal ethylene selectivities in the range of 75–85% at high degrees of acetylene conversion and hint at the crucial role of hydrogen dissociation on the overall process. Density-functional theory is applied to CeO₂(111) in order to investigate reaction intermediates and to calculate the enthalpy and energy barrier for each elementary step, taking into account different adsorption geometries and the presence of potential isomers of the intermediates. At a high hydrogen coverage, β-C₂H₂ radicals adsorbed on-top of surface oxygen atoms are the initial reactive species forming C₂H₄ species effectively barrierless. The high alkene selectivity is owed to the lower activation barrier for subsequent hydrogenation leading to gas-phase C₂H₄ compared to that for the formation of β-C₂H₄ radical species. Moreover, hydrogenation of C₂H₄ species, if formed, must overcome significantly large barriers. Oligomers are the most important byproduct of the reaction and they result from the recombination of chemisorbed C₂H₂ species. These findings rationalize for the first time the applicability of CeO₂ as a catalyst for olefin production and potentially broaden its use for the hydrogenation of polyunsaturated and polyfunctionalized substrates containing triple bonds.

1. INTRODUCTION

The partial hydrogenation of alkenes to alkenes is a crucial step for the purification of olefin streams in the petrochemical industry as well as for the manufacture of fine chemicals.¹,² To this end, a high degree of product selectivity is required. Prototypical heterogeneous catalysts to perform this reaction are based on palladium.³ This metal is highly active at moderate temperature and hydrogen pressure but often suffers from suboptimal selectivity and lifetime due to alkane and oligomer formation.⁴⁻⁶ For this reason, the development of novel materials excelling the performance of palladium-based systems constitutes a key challenge requiring identification of active sites and molecular-level understanding of the associated reaction mechanisms.⁶⁻¹⁰

The recent discovery that CeO₂ exhibits a remarkable selectivity in the partial gas-phase hydrogenation of alkenes¹¹ has opened exciting perspectives in catalysis research. In the past, ceria was applied in the formulation of various alkyne and alkadiene hydrogenation catalysts, acting as a promoter or stabilizer and most commonly as a carrier of noble metal nanoparticles.¹²⁻¹⁴ However, its stand-alone ability to catalyze these reactions has never been stated before. With a propene selectivity of 91% at ca. 100% propyne conversion,¹¹ ceria is one of the most effective catalysts ever reported for this family of reactions. In contrast to that, other reducible oxides such as TiO₂ and ZnO were inactive in the gas-phase hydrogenation of alkenes under similar conditions.¹¹ A high surface area and the absence of oxygen vacancies are beneficial for attaining high catalytic performances. Additionally, a large hydrogen excess in the feed mixture and temperatures above 473 K are required, strongly suggesting that hydrogen splitting is the rate-limiting step. These results have been recently confirmed and generalized for the partial hydrogenation of other functional groups, including substituted nitroarenes.¹⁵ However, a sound mechanistic insight into partial hydrogenation by ceria, which includes the determination of the relevant reaction pathways, does not yet exist. This knowledge is vital to rationalize the
origin and uniqueness of the highly selective character of CeO$_2$ for olefin production as well as to devise its potential applicability for the liquid-phase hydrogenation of polyfunctionalized substrates containing triple bonds.

In this work, we focus on elucidating the mechanism for the partial (and full) hydrogenation of acetylene to ethylene (and ethane) over the pristine—most stable and exposed—CeO$_2$(111) surface. Ethylene stands at the basis of the chemical industry and is involved in the production of a wide range of solvents, raw materials for paints, elastomers, thermoplastics, and synthetic fibers. Our catalytic experiments over polycrystalline CeO$_2$ indeed confirm that the reaction rate increases quasi-linearly with increasing the partial pressure of hydrogen, attaining an ethylene selectivity of up to 85%. Prereduction in H$_2$ linearly with increasing the partial pressure of hydrogen, and synthetic solvents, raw materials for paints, elastomers, thermoplastics, and industry and is involved in the production of a wide range of metal oxides, and speciﬁcally reducible oxides such as ceria, has been yet attempted in hydrogenation catalysis. In addition, the innumerable theoretical studies modeling metal surfaces (mostly Pd, Ni, Cu, Au, Ag, and Ni–Zn$^{8,9,18–32}$) for alkyne hydrogenation, no investigations over metal electrodes of the CeO$_2$ catalyst (c).

Figure 1. XRD pattern (JCPDS 65-5923 as reference in gray) (a), HRTEM micrograph (b), and H$_2$-TPR profile of the CeO$_2$ catalyst (c).

2. EXPERIMENTAL SECTION

Materials and Catalator Characterization. Commercial CeO$_2$ nanopowder (Aldrich, ref: 544841) of high purity with a nominal total surface area of 70 m$^2$ g$^{-1}$ was calcined in static air at 673 K for 5 h and eventually prereduced in flowing hydrogen (42 cm$^3$ min$^{-1}$, 5 vol.% H$_2$/He) at 673 K for 30 min (heating rate = 5 K min$^{-1}$). Powder X-ray diffraction (XRD) was acquired in a PANalytical X’Pert PRO-MPD diffractometer equipped with Bragg–Brentano geometry and Ni-filtered Cu K$_\alpha$ radiation ($\lambda = 0.1541$ nm). Data were recorded in the 2$\theta$ range of 5–70$^\circ$, with an angular step size of 0.017$^\circ$ and a counting time of 0.26 s per step. Chemical composition analyses were carried out by inductively coupled plasma optical emission spectroscopy (ICP-OES) on a Horiba Ultra 2 instrument equipped with photomultiplier tube detection. High-resolution transmission electron microscopy (HR-TEM) was undertaken on a FEI Tecnai F30 microscope operated at 300 kV. Temperature-programmed reduction in hydrogen (H$_2$-TPR) was carried out in a Thermo TPD/R/O 1100 unit equipped with a thermal conductivity detector. The catalyst (ca. 50 mg) was loaded in the quartz microreactor (11 mm i.d.), pretreated in helium (20 cm$^3$ min$^{-1}$) at 473 K for 30 min, and cooled down to 323 K in He. The analysis was carried out in 5 vol.% H$_2$/N$_2$ (20 cm$^3$ min$^{-1}$) at 473 K for 30 min. Temperature, and partial H$_2$ pressure were varied in the range of 0.12–1 s, 423–623 K, and 250–750 mbar (H$_2}$/C$_2$H$_2$ = 10–30), respectively, using He as the balance gas. All the catalytic data were measured
under steady-state conditions and the performance was stable for several hours on stream. The fulfillment of relevant criteria was verified in order to discard mass-transport limitations. In addition, the temperature gradients along the bed, measured as the difference between the temperature at the outlet of the bed and the oven temperature, were <5 K, enabling quasi-isothermal operation. The composition of the gas at the reactor outlet was analyzed by an online gas chromatograph (Agilent GC7890A) equipped with a GS-GasPro column and a flame ionization detector. The conversion of acetylene, $X(C_2H_2)$, was determined as the amount of reacted alkene divided by the amount of alkene at the reactor inlet. The turnover frequency was expressed as millimole of C$_2$H$_4$ divided by the amount of alkyne at the reactor inlet. The moles of surface oxygen were calculated as the product of the mass of the catalyst multiplied by the surface oxygen density and by the surface area, and divided by the Avogadro number. Particularly, the surface oxygen density in polycrystalline CeO$_2$ was calculated taking into account the density of surface oxygen on each facet and their relative abundance in the XRD pattern (Figure 1a), assuming that all faces contribute equally to the activity of CeO$_2$. The selectivity to ethylene, $S(C_2H_4)$, and ethane, $S(C_2H_6)$, were calculated as the quantity of product formed divided by the amount of converted alkene. The selectivity to oligomers was determined as $S(\text{OL}) = 1 - S(C_2H_4) - S(C_2H_6)$.

3. THEORETICAL METHODS

Spin-polarized DFT and supercell periodic models were used as implemented in the Vienna ab initio simulation package (VASP). We treated explicitly the C (2s, 2p), O (2s, 2p), and Ce (4f, 5s, 5p, 5d, 6s) electrons as valence states expanded in plane-waves with a cutoff energy of 400 eV, whereas the remaining electrons were replaced by Perdew–Burke–Ernzerhof (PBE)-based projector-augmented wave (PAW) potentials. Total energies and electron densities were computed using the DFT+U approach of Dudarev et al. in which a Hubbard U-like term describing the onsite Coulomb interactions ($U_{\text{eff}} = U - J$, that is, the difference between the Coulomb $U$ and exchange $J$ parameters, hereinafter referred to as simply $U$) is added to the PBE generalized-gradient approximation (GGA) functional. We used a value of $U = 4.5$ eV for Ce atoms, which was calculated self-consistently by Fabris et al. using a linear response approach. A Monkhorst–Pack grid with $6 \times 6 \times 1$ k-point sampling per (1 $\times$ 1) surface unit cell was used.

The O-terminated CeO$_2$(111) surface with (3 $\times$ 3) periodicity was modeled using a supercell, containing six atomic layers separated by at least 12 Å of vacuum. All the atoms in the three bottom layers of the slab were fixed at their PBE+U bulk-truncated ($a_{\text{cell}} = 5.485$ Å) positions during geometry optimization, whereas the rest of atoms were allowed to fully relax. The calculations of gas-phase species (H$_2$, C$_2$H$_2$, C$_2$H$_4$, and C$_2$H$_6$) were performed with Γ-point sampling using at least $12 \times 12 \times 12$ Å$^3$ boxes. For all the systems investigated, a range of different initial positions and orientations was considered, and the structures were relaxed using a conjugate-gradient algorithm with a residual force threshold of 0.05 eV Å$^{-1}$.

All reported adsorption energies were calculated in relation to the corresponding gas-phase molecule and the bare CeO$_2$(111) surface, implying that negative reaction energies correspond to exothermic processes. We found that the adsorption of H or C$_2$H$_4$ species on the CeO$_2$(111) surface results in the formation of one Ce$^{3+}$ ion per adsorbed species. It is known that such Ce$^{3+}$ ions are likely to be more stable on the first cationic layer of the CeO$_2$(111) surface. Imposing this as a constrain, we systematically explored a range of possible configurations for the location of Ce$^{3+}$ ions upon adsorption of a given species. This search revealed relative energy differences between the global minima and other possible locations of Ce$^{3+}$ ions as large as 130 meV/Ce$^{3+}$, i.e., up to 390 meV when a maximum of three Ce$^{3+}$ ions are present (Figure S1 in Supporting Information). Consequently, all minima reported in the following correspond to the lowest-energy Ce$^{3+}$ ion configurations found. To determine the electronic ground state we used a self-consistent-field minimization algorithm as applied in ref 25 and acknowledge the challenge for DFT+U to find the global minimum with respect to 4f orbital occupations. We noticed that only high-spin (ferromagnetic-like) states were considered for the sake of simplicity. This assumption is reasonable, since the energy difference between the high-spin state and any other spin state is very small, typically less than 10 meV.

Vibrational frequencies were obtained numerically by building the Hessian dynamical matrix through finite atomic displacements of 0.01 Å from the optimized structures. After diagonalization of the Hessian matrix, the corresponding harmonic frequencies associated to each normal vibrational mode were obtained. Transition structures (TS) for the considered reaction paths were located by employing the nudged elastic band (NEB) algorithm using at least five images along each pathway. Harmonic vibrational frequency analysis showed that all TS structures had only one imaginary frequency.

4. RESULTS AND DISCUSSION

Characterization of CeO$_2$ and Hydrogenation Performance. The X-ray diffraction pattern in Figure 1a shows that CeO$_2$ is the only crystalline phase in the commercial sample. HR-TEM in Figure 1b shows that the ceria nanoparticles primarily expose (111) facets with an interplanar spacing of 0.337 nm. ICP-OES analyses confirmed the high purity of the sample, which contains no trace of conventional hydrogenation metals such as Pd, Pt, Au, and Ni. Catalytic tests assessing the influence of temperature and H$_2$/C$_2$H$_2$ ratio on the activity and selectivity were conducted (Figure 2). Raising the temperature from 423 to 623 K (Figure 2a), the acetylene conversion reached a maximum (84%) at 473–523 K. The lower conversion above 523 K was attributed to the detrimental effect of surface CeO$_2$ reduction, which starts at 523 K, implying that H$_2$ dissociation is rate limiting. At H$_2$/C$_2$H$_2$ = 10 and 523 K, the highest turnover frequency (TOF) was obtained, corresponding to 0.3 mmol C$_2$H$_4$ mol$^{-1}$ CeO$_2$ s$^{-1}$. This value is comparable to the intrinsic activity of Ag-based catalysts in hydrogenation.

The selectivity to ethylene increases from 73% at H$_2$/C$_2$H$_2$ = 10 to 80% at H$_2$/C$_2$H$_2$ = 20, and remains unchanged at a higher ratio. The selectivity to ethane did not
exceed 10%. At low hydrogen coverage (H₂/C₂H₂ ≤ 15), extensive oligomerization takes place. At high coverage, the addition of hydrogen in the feed suppresses undesired pathways, pointing to a decisive role of H₂ dissociation in the reaction mechanism for maximizing the alkene production. Finally, upon increasing the conversion of acetylene at fixed T and H₂/C₂H₂ ratio (Figure 2c), a reduced selectivity to ethylene was observed, with the concomitant increase in oligomer formation. This result suggests that ethylene partakes in the oligomerization pathway. At optimal reaction conditions (T = 523 K, H₂/C₂H₂ = 30, τ = 0.35 s), a stable selectivity to ethylene of ca. 80% at a degree of acetylene conversion of ca. 80% was attained; this result excels the typical performance of conventional hydrogenation catalysts (typically, at a similar degree of conversion, the ethylene selectivity is 50−75%).

The influence of the presence of oxygen vacancies (formed by extensive prereduction of ceria in H₂ and quantified by infrared spectroscopy) on the catalytic performance is depicted in Figure 3. On the oxidic catalyst (no pretreatment in H₂ flow), a high acetylene conversion and ethylene selectivity have been attained. Upon prereduction of CeO₂ in 5 vol.% H₂/He at 673 K, oxygen vacancies are created, and a drop in the acetylene conversion and ethylene selectivity is observed. Therefore, this result points to the detrimental role of ceria reduction, suggesting that oxygen atoms are active centers for the adsorption of reactants and intermediates.

**Acetylene Activation.** The fact that ceria predominantly exposes (111) facets and nonreduced surfaces are beneficial for the hydrogenation of alkynes accounts for the choice of CeO₂(111) as the model catalytic surface.

The molecular adsorption of hydrocarbon molecules on CeO₂(111) is expected to be very weak and dominated by van der Waals dispersion forces. Indeed, the PBE+U adsorption of C₂H₂ on CeO₂(111) is only −0.10 eV. Furthermore, the adsorption of C₂H₂ as a radical species on-top of a surface oxygen atom is exothermic (−0.12 eV), with the unpaired electron localized on the β carbon⁴⁴ (Figure 4a). The electron removed from such β-C₂H₂ species yields to the formation of one Ce³⁺ ion. Radicals are generally short-lived and highly reactive. As discussed below, these species play a crucial role in the selective hydrogenation to C₂H₄ at high H₂ coverage. In addition, they are likely to promote the formation of oligomers at low H₂/C₂H₂ ratios.

In the case of C₂H₂, our PBE+U calculations show that dissociative heterolytic adsorption (Figure 4b) on CeO₂(111) is endothermic by 0.38 eV with respect to the gas-phase C₂H₂ molecule. Notwithstanding, dissociative homolytic adsorption is strongly exothermic (−1.77 eV) and, therefore, the adsorption mechanism for C₂H₂ on CeO₂(111) leads to the formation of an acetylide (H−C≡C) and a H species on top of two adjacent
such vibrational modes for the homolytic adsorption structure: These experimental values agree well with the PBE+

times), surface O sites become saturated and C2H2 might start

This result suggests that at high coverage (longer exposure

provide further evidence for the homolytic dissociation pathway. After 20 min exposure time, the bands at 3708

cm−1 and 2160 cm−1 are assigned to the stretching modes of monocoordinated O−H and H−C≡C species, respectively. These experimental values agree well with the PBE+U values of such vibrational modes for the homolytic adsorption structure: 3702 cm−1 and 2153 cm−1, respectively. Interestingly, after 80 min exposure time, the absorption at 3080 cm−1 gains intensity; this band is in reasonable good agreement with the computed O−H stretching mode for heterolytic adsorption (3110 cm−1).

The infrared spectra of C2H2 adsorbed on CeO2 in Figure 5

Figure 5. Infrared spectra of CeO2 in He (20 cm3 min−1) and after 20 and 80 min of exposure to 5 vol% C2H2/He (20 cm3 min−1). The spectra were recorded at 523 K in the absence of gas-phase H2.

reaction can proceed toward the coadsorption of C2H3

Each asterisk denotes a clean CeO2(111) surface. Reactants, intermediates, and products that are followed by an asterisk stand for adsorbed species (our DFT structure optimizations show that the adsorption of all considered species takes place preferentially on top of surface O atoms). Species in parentheses and separated by commas indicate coadsorbed species on nearby active surface O sites.

We have arbitrarily assumed that H2 physisorption and subsequent dissociation, eqs R1 and R2, are the initial steps instead of the adsorption of a gas-phase C2H2 molecule, eq R4. This assumption is actually meaningful because high acetylene conversion rates are only achieved under experimental conditions when H2 is in high excess in relation to acetylene; indeed this is a strong indication that the dissociation of hydrogen is the limiting step of the whole process. Consequently, the reaction starts with the physisorption of H2 (eq R1) followed by homolytic dissociative chemisorption to leave two H* species (eq R2) and release 2.35 eV. The two H atoms adsorb on top of two nearest neighbor surface O atoms to form two hydroxyl groups and two Ce3+ (Figure S2 in Supporting Information). This elementary step is hindered by an energy barrier of 1.00 eV. Previous DFT+U calculations reported a much lower barrier (0.22 eV). However, using their reported TS structure and their computational setup, we found the structure to be unstable. Nonetheless, this higher activation energy is compatible with the high H2 pressures needed for conversion. The separation of two nearest neighbor H* species leading to two isolated species, (H,H)* → H* + H*, is thermodynamically slightly unfavorable by 0.07 eV (eq R3). The reaction continues with the adsorption of an acetylene molecule near to one hydroxyl group (eq R4) to form (β-C2H2,H)* (inset D in Figure 6). This step is energetically favored by only 0.15 eV. Then such radical species can readily react with the nearby hydroxyl group leading to the formation of a C2H2* and releasing 1.48 eV. In addition, this process has a barrier of only 0.09 eV. At this stage, the reaction can proceed toward the coadsorption of C2H2* and H* species via eq R6 and the formation and release of a gas-phase ethylene molecule (eq R7), resulting in an overall partial hydrogenation process. This last elementary step is substantially endothermic by 1.65 eV and presents a large energy barrier of 2.86 eV. Although this energy barrier for the formation of
Figure 6. Reaction energy profile for acetylene hydrogenation on CeO$_2$(111). All energies are referenced to the total energy of H$_2$(g), C$_2$H$_2$(g), and the clean CeO$_2$(111) surface (state A). States A–L stand for minima and their structures are schematically shown in the insets, whereas transition structures are indicated by R2–R17 (see Figures S2–S5 for more details). Colors indicate different pathways: partial hydrogenation of acetylene to ethylene via R5 (black line) or via dissociative acetylene adsorption (light brown), and total hydrogenation to C$_2$H$_6$ (red line).

Table 1. Reaction Energies ($E_r$) and Activation Energies of Forward ($E_{a,f}$) and Backward ($E_{a,b}$) Reactions in eV for the Elementary Steps Involved in the Hydrogenation of Acetylene on CeO$_2$(111)

<table>
<thead>
<tr>
<th>eq</th>
<th>reaction</th>
<th>$E_r$</th>
<th>$E_{a,f}$</th>
<th>$E_{a,b}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>H$_2$ + * → H$_2^*$</td>
<td>0.00</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>R2</td>
<td>H$_2^<em>$ → (H,H)$^</em>$</td>
<td>-2.35</td>
<td>1.00</td>
<td>3.35</td>
</tr>
<tr>
<td>R3</td>
<td>(H,H)$^<em>$ → H$^</em>$ + H$^*$</td>
<td>0.07</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>R4</td>
<td>H$^<em>$ + C$_2$H$_2$ → (β-C$_2$H$_3$H)$^</em>$</td>
<td>-0.15</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>R5</td>
<td>(β-C$_2$H$_3$H)$^<em>$ → C$_2$H$_4^</em>$</td>
<td>-1.48</td>
<td>0.09</td>
<td>1.58</td>
</tr>
<tr>
<td>R6</td>
<td>H$^<em>$ + C$_2$H$_2$ → (C$_2$H$_4$H)$^</em>$ + *</td>
<td>0.01</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>R7</td>
<td>(C$_2$H$_4$H)$^<em>$ → C$_2$H$_4^</em>$</td>
<td>1.65</td>
<td>2.86</td>
<td>1.20</td>
</tr>
<tr>
<td>R8</td>
<td>(β-C$_2$H$_4$H)$^<em>$ → (C$_2$H$_4$H)$^</em>$ + *</td>
<td>-1.73</td>
<td>0.74</td>
<td>2.47</td>
</tr>
<tr>
<td>R9</td>
<td>(C$_2$H$_4$H)$^<em>$ → (α-C$_2$H$_3$H)$^</em>$</td>
<td>1.22</td>
<td>1.47</td>
<td>0.25</td>
</tr>
<tr>
<td>R10</td>
<td>(α-C$_2$H$_3$H)$^<em>$ → C$_2$H$_4^</em>$</td>
<td>-0.97</td>
<td>0.54</td>
<td>1.51</td>
</tr>
<tr>
<td>R11</td>
<td>(C$_2$H$_4$H)$^<em>$ → β-C$_2$H$_4^</em>$</td>
<td>2.13</td>
<td>3.65</td>
<td>1.52</td>
</tr>
<tr>
<td>R12</td>
<td>H$_2$ + * → H$_2^*$</td>
<td>0.00</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>R13</td>
<td>H$_2^<em>$ → (H,H)$^</em>$</td>
<td>-2.35</td>
<td>1.00</td>
<td>3.35</td>
</tr>
<tr>
<td>R14</td>
<td>(H,H)$^<em>$ + β-C$_2$H$_2$ → H$^</em>$ + (β-C$_2$H$_3$H)$^*$</td>
<td>-0.01</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>R15</td>
<td>(β-C$_2$H$_3$H)$^<em>$ → C$_2$H$_4^</em>$</td>
<td>-1.03</td>
<td>0.41</td>
<td>1.44</td>
</tr>
<tr>
<td>R16</td>
<td>H$^<em>$ + C$_2$H$_2$ → (C$_2$H$_4$H)$^</em>$ + *</td>
<td>-0.04</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>R17</td>
<td>(C$_2$H$_4$H)$^<em>$ → C$_2$H$_4^</em>$ + *</td>
<td>1.20</td>
<td>3.44</td>
<td>2.25</td>
</tr>
<tr>
<td>R18</td>
<td>(C$_2$H$_4$B,C$_2$H$_3$H)$^<em>$ → δ-C$_2$H$_4^</em>$</td>
<td>-0.73</td>
<td>0.42</td>
<td>1.15</td>
</tr>
</tbody>
</table>

It is important to realize that, although this alternative pathway initially involves the thermodynamically preferred dissociative adsorption of acetylene (eq R8) releasing 1.73 eV, it is kinetically more energy-demanding than the pathway via β-C$_2$H$_3$H$^*$ (eq R5). In particular, eq R8 is hindered by an activation energy of 0.74 eV, whereas in eq R5 the reaction proceeds almost without energy barrier (Table 1). Interestingly, it is the high reactivity of β-C$_2$H$_3$H$^*$ species toward hydrogenation by nearby H$^*$ species what activates the formation of the key C$_2$H$_4^*$ species for the subsequent hydrogenation process, avoiding the thermodynamic preference for dissociative adsorption of isolated acetylene molecules.

Once a surface C$_2$H$_3^*$ species is formed, the reaction can proceed toward the formation and desorption of a gas-phase C$_2$H$_4$ molecule (eq R7), resulting in an overall partial hydrogenation process. Alternatively, the adsorbed C$_2$H$_3^*$ species can be hydrogenated to ethene via the formation of a β-C$_2$H$_4^*$ radical on the surface (inset I in Figure 6). The list of elementary steps leading to the complete hydrogenation process is:

$$ H_2 + (C_2H_3H)^* + * \rightarrow H_2 + \beta-C_2H_3^* + * $$  \hspace{1cm} (R11)

$$ H_2 + \beta-C_2H_4^* + * \rightarrow H_2^* + \beta-C_2H_4^* $$  \hspace{1cm} (R12)

ethylene is 1.86 eV larger than for the dissociation of H$_2$ (eq R2), overall the TS of R7 lies approximately 1.2 eV below the TS of R2 in the reaction energy profile (Figure 6). This is consistent with the experimental fact that hydrogen splitting was the limiting step.

We also considered an alternative reaction pathway to eq R5 to form C$_2$H$_4^*$ species via the dissociative adsorption of acetylene (inset G in Figure 6) and the formation of a β-C$_2$H$_3^*$ isomer, a α-C$_2$H$_3^*$ radical species:

$$ H_2 + (\beta-C_2H_3H)^* + H^* \rightarrow H_2 + (\beta-C_2H_3H)^* + H^* $$  \hspace{1cm} (R8)

$$ H_2 + (C_2H_3H)^* + H^* \rightarrow H_2 + (\alpha-C_2H_3H)^* + H^* $$  \hspace{1cm} (R9)

$$ H_2 + (\alpha-C_2H_3H)^* + H^* \rightarrow H_2 + C_2H_4^* + H^* $$  \hspace{1cm} (R10)
H₂* + β-C₂H₄* → (H₂H)* + β-C₂H₄*  (R13)
(H₂H)* + β-C₂H₄* → H₂* + (β-C₂H₄H)*  (R14)
H* + (β-C₂H₂H)* → H* + C₂H₅*  (R15)
H* + C₂H₅* → (C₂H₅H)* + *  (R16)
(C₂H₅H)* + * → C₂H₇ + 2*  (R17)

Essentially, the reactions to form gas-phase C₂H₄ or β-C₂H₄* from C₂H₅* and H* species compete with each other (eqs R7 and R11, respectively). These two elementary steps present large energy barriers, but the pathway leading to gas-phase C₂H₄ is hindered by a substantially smaller activation energy, 2.86 eV, than the formation of β-C₂H₄*, 3.65 eV, which is kinetically less favorable (Table 1). The most energy-demanding step toward complete hydrogenation provides, therefore, an explanation to the experimentally observed strong ethylene selectivity. In addition, a selective catalyst is expected to offer a high (low) stability of adsorbed acetylene (ethylene), i.e., thermodynamic selectivity. This qualitative requirement is actually consistent with our results. Comparing states I and F in Figure 6, the adsorption of gas-phase ethylene (state F) to form an activated adsorbed ethylene molecule on the surface (state I) is indeed an endothermic process by 0.5 eV, whereas the activation of a gas-phase acetylene to form a β-C₂H₄* species (state D) is slightly exothermic by 0.15 eV (eq R4). Therefore, a gas-phase ethylene molecule formed in eq R7 is not thermodynamically prone to be readsorbed on the surface.

Complete hydrogenation from C₂H₅* species through the formation of a β-C₂H₄* radical (eq R11) requires the physisorption and subsequent dissociation of a second H₂ molecule on the CeO₂(111) surface (eqs R12 and R13). Coadsorbing H* and β-C₂H₄* species on nearby O surface atoms is thermo-neutral. The overall (C₂H₅H)* + H* → (β-C₂H₄H)* process is slightly exothermic by 0.22 eV. The β-C₂H₄* radical can readily react with a nearby H* releasing 1.03 eV and with an activation energy of only 0.41 eV (eq R15). This process leads to the formation of very stable C₂H₅* species. Bringing together C₂H₅* and H* is slightly favorable by 0.04 eV (eq R16). Forming the final complete hydrogenation product, ethane, by the reaction of C₂H₅* with the coadsorbed H* (eq R17) is endothermic by 1.20 eV. In addition, this final hydrogenation step presents a large activation energy (3.44 eV), which hampers the reaction toward ethane and explains the very low selectivity to the overhydrogenated product observed experimentally.

As discussed above, the maximum selectivity to oligomers is actually higher than that to ethane (Figure 2a,b), and it is mostly ethylene participating in the production of oligomers (Figure 2c). Specifically, ethylene precursors (C₂H₅*) are very stable surface species, as pointed out by the corresponding deep potential well of state D in Figure 6. Hence, such species are expected to exhibit long resident times on the ceria surface. At low coverages, C₄ oligomers may result, for example, from direct coupling of C₂H₅* with a nearby β-C₂H₂* radical according to the following process:

(C₂H₅β-C₂H₂)* → δ-C₄H₅*  (R18)

This reaction is moderately exothermic by 0.73 eV and is hindered by an activation energy of only 0.42 eV as shown in Table 1. Notice that the product of eq R18, δ-C₄H₅*, is a radical, which can presumably be release as a C₄ oligomer after reacting with nearby H* or evolve to a larger oligomer by attaching an extra C₄H₅* species, although such reaction pathways have not been explored here.

Interestingly, though, compared with the formation of ethylene (eq R7), oligomerization via C₂H₅ and β-C₂H₄ is largely preferred (Figure 7). It is important to stress that each C₂H₅* species is surrounded by six nearby O surface atoms (Figure S6 in the Supporting Information); for oligomerization to occur, a second C₂H₅* species should be adsorbed on one of these six neighboring active sites, otherwise the separation between the two species is too large (>3.5 Å) for species to react. Since hydrogen competes for the same adsorption sites, the observed gradual decrease in oligomer production when increasing the H₂/C₂H₂ ratio can be linked to the fact that an excess of H* surrounding C₂H₅* species blocks the energetically more favorable oligomerization process, facilitating the conversion toward ethylene instead. This blocking effect is supported by the fact that surface H diffusion is hindered by a large energy barrier and, therefore, H mobility is expected to be low even at high temperatures. We should emphasize that other oligomerization reactions could also be proposed. We have focused here only on the recombination of C₂H₅ and β-C₂H₄ (eq R18) because this is likely one of the most relevant oligomerization processes, but, for example, species such as β-C₂H₅* may actuate the oligomerization as well, which is expected to compete with ethane formation along the last steps of the complete hydrogenation process (from eq R11 to eq R17). A detailed study of oligomerization mechanisms is out of the scope of this work, however.

It is important to realize that the adsorption of C₂H₅* and H* intermediate species involves the reduction of the surface. It is precisely the ability of CeO₂ for easily accommodating one electron into Ce 4f states that facilitates the stabilization of β-
C\textsubscript{2}H\textsubscript{4} radicals, a key reaction intermediate in the overall hydrogenation process. In addition, each elementary hydrogenation step (C\textsubscript{2}H\textsubscript{2}H\textsubscript{2}) \rightarrow (C\textsubscript{2}H\textsubscript{4}H\textsubscript{2}) implies the reoxidation of a Ce\textsuperscript{3+} ion. Thus the reversibility of the Ce\textsuperscript{3+} ↔ Ce\textsuperscript{4+} process is vital for understanding the outstanding hydrogenation properties of CeO\textsubscript{2}.

As for the detrimental effect of oxygen vacancies on the reactivity, we find that all reactants and intermediate species involved in the reaction adsorbed on-top of surface O sites. Hence, the creation of oxygen vacancies upon strong pretreatment in H\textsubscript{2} at 673 K simply reduces the number of active sites.

5. CONCLUSIONS

Acetylene hydrogenation on polycrystalline ceria proceeds with very high selectivity to ethylene. Oligomers are the major byproduct (maximum 16\%) and result from C=C couplings of C\textsubscript{2}H\textsubscript{4} radicals. DFT simulations on CeO\textsubscript{2}(111) substantiate the experimental observations and provide molecular-level insight in the active sites and reaction mechanism. Ethylene formation is the reaction that is most likely to occur when C\textsubscript{2}H\textsubscript{2} and H\textsubscript{2} are coadsorbed on neighboring surface oxygen sites of the CeO\textsubscript{2}(111) surface, as it is well favored over the formation of β-C\textsubscript{2}H\textsubscript{4} radical species that would enable subsequent hydrogenation. Acetylene adsorption leads to the formation of highly reactive β-C\textsubscript{2}H\textsubscript{4} radical species that are hydrogenated to form C\textsubscript{2}H\textsubscript{4} with no barrier at large H\textsubscript{2}/C\textsubscript{2}H\textsubscript{2} ratios, and are likely to form oligomers at low ratios. Finally, the formation of ε-C\textsubscript{2}H\textsubscript{4} radical species that would enable subsequent hydrogenation.

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(44) The a refers to the first carbon that attaches to an surface O atom. By extension, the second carbon is the β carbon.
