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Influence of the Variation in the Hubbard Parameter (U) on Activation Energies of CeO_2 -Catalysed Reactions

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Abstract

Accurate description of thermodynamic, structural and electronic properties for bulk and surfaces of ceria (CeO_2) necessitates the inclusion of the Hubbard parameter (U) in the density functional theory (DFT) calculations to precisely account for the strongly correlated $4f$ electrons. Such treatment is a daunting task when attempting to draw a potential energy surface for CeO_2 -catalyzed reaction. This is due to the inconsistent change in thermo-kinetics parameters of the reaction in reference to the variation in the U values. As an illustrative example, we investigate herein the discrepancy in activation and reaction energies for steps underlying the partial and full hydrogenation of acetylene over the $\text{CeO}_2(111)$ surface. Overall, we find that both activation and reaction energies positively correlate with the increase in the U value. In addition to benchmarking against more accurate theoretical methodologies, we suggest that U values are better to be optimized against kinetics modelling of experimentally observed profiles of products from the catalytic-assisted system of reactions.

Keywords: Ceria, DFT + U ; reaction barriers; hydrogenation of acetylene; catalysts; transition state; Hubbard Parameter (U)

1. Introduction

Cerium oxide (CeO_2 , ceria) and its based materials are essential in many strategic catalytic industrial applications [1-3]. As oxygen –storage ingredients [4], they are utilized in three-way catalysts (TWC) formulations [5]. In the latter, ceria acts as an oxidizing and reducing agent for some pollutants (CO , NO_x , HC) emitted by cars and subsequently converting them to harmless materials. Another catalytic application of ceria is that the ceria– supported transition metals are being presently considered as active catalysts for the water- gas - shift reaction which converts CO and water into CO_2 and hydrogen [6]. The fact standing behind these and other applications of ceria is the two stable and extreme oxidation states [7] namely, Ce^{+4} , Ce^{+3} . As such cerium oxide may occupy different possible states between these two ultimate oxidation states; CeO_x .

Accurate electronic, structural and thermo-mechanical properties of materials can now be readily acquired by density functional theory (DFT) calculations. However, plain DFT functional suffer from a serious shortcoming in describing the electronic structure of ceria. Excessive delocalisation of the $4f$ electron incorrectly results in a metallic behaviour for CeO_2 , in contrast to its semiconducting nature observed experimentally (band gap of ceria amounts to 6 eV [8]). To force localisation and strong correlation in the $4f$ electrons in ceria, the DFT + U (Hubbard parameter) approach has been widely deployed. In this approach, the empirical Hubbard U potential treats the well-established deficiencies of pure DFT methods in accurately accounting for the strongly correlated $4f$ electrons in lanthanides in general [9]. Unfortunately, there is no single U value that can reproduce all materials attributes, such as geometries, thermodynamics and density of states. The U value for bulk CeO_2 is often optimized against its lattice constant, enthalpy of formation and band gap. Several literature studies [10, 11] have thoroughly studied the effect of the U parameter on the electronic properties of CeO_2 surfaces. These studies have mainly surveyed the change in the electronic band gap of bulk CeO_2 with the U parameter attaining an optimal value that corresponds to the experimentally measured electronic distribution profiles.

33 The U value also displays sensitivity toward the deployed DFT functional. As such, an
34 optimized U value for enthalpy of formation or band gap may not represent the optimum value
35 for acquiring thermo-kinetic parameters for ceria-catalysed reactions. Computing accurate
36 activation energies is a central task in computational catalysis. Previous computational studies
37 on catalytic reactions over ceria have mainly deployed the U value optimized for bulk's band
38 gap. For instance, Chen, *et al.* [12] reported reaction pathways for the reduction of $\text{CeO}_2(111)$
39 and $\text{CeO}_2(110)$ surfaces via interaction with gaseous by H_2 molecules utilizing a U value of 7.1
40 eV based on the PW91 functional. Likewise, in recent study [13], we deployed a DFT + U
41 functional to report reduction energies for pure CeO_2 and CeO_2 alloyed with Zr and Hf at
42 various loading ratios. We optimized our deployed U value against the experimental value for
43 the complete reduction of ceria at 298. 15 K ($2\text{CeO}_2 \rightarrow \text{Ce}_2\text{O}_3 + 1/2\text{O}_2$).

44

45 To this end, the aim of this contribution is to survey the change in reaction and activation
46 energies for a set of well-studied systems of reaction when deploying different values of U .
47 Herein, we limit our analysis to energy terms, however, it must also be noted that geometrical
48 as well as electronic factors must also be considered when locating an optimal U value for a
49 given reaction.

50

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52 **2. Methodology**

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54 Herein, geometry optimizations and energy calculations were carried out at absolute zero via
55 the plane-wave DFT program of the Vienna ab initio simulation package (VASP) [14]. The
56 calculations methodology comprises a spin-polarized PAW-PBE functional [15], van der
57 Waals correction by the Grimme functional [16], and a Gaussian smearing. For Ce, it is
58 necessary to apply on-site Coulomb interaction correction (DFT+ U), to account and correct f
59 electron delocalisation. The DFT+ U formalisms suggested by Dudarev *et al.* [9]. has been
60 applied. This method was proven to yield band gap, lattice constant and heat of formation in
61 a close agreement with the analogous experimental values. It has been shown including van
62 der Waals corrections for species adsorption over ceria surfaces systematically increases
63 adsorption energies [2]. Magnetic moment orientation has also been considered, but it is not
64 sensitive to pristine CeO_2 , as it is a nonmagnetic insulator material [17]. Integration over the

65 Brillouin - zone was performed using Monkhorst - pack grids of $4 \times 4 \times 4$ and $4 \times 4 \times 1$ κ -
66 points for the bulk and surface $\text{CeO}_2(111)$ calculations, respectively [18]. Structural
67 optimisation calculations deploy a plane wave cut off energy of 400 eV, an energy tolerance of
68 0.1 meV and atomic force tolerance of 0.05 eV/Å. Nudged elastic band (NEB) utilized in
69 transition state calculations uses the same plane wave cut off energy and energy tolerance.

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72 **3. Results and Discussions**

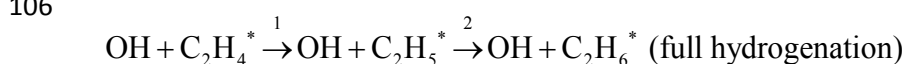
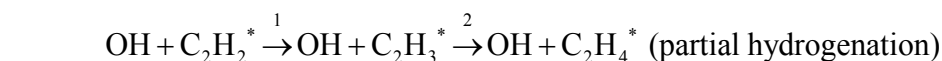
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74 The seminal work by Capdevila-Cortada *et al.* [19]. has systematically analysed the effect of
75 the U parameter on the activation and reaction energy for the first hydrogen stripping of
76 formaldehyde into adsorbed CHO and OH. Author finds that the influence of the variation in
77 the U value is more evident when there is a reduction in the oxidation state of cerium surface
78 atoms upon interaction/dissociative adsorption of gas phase species. Thus, the change in the
79 U value exerts no change in the physisorption energy of formaldehyde over the $\text{CeO}_2(111)$
80 surface. Likewise, the change in activation and reaction energy when a small U value is
81 employed was a rather very minimal. Indeed, at small values of U , the f electrons of Ce atoms
82 are still delocalized. However, at higher values of U (3.0 – 6.0 eV), both activation and reaction
83 energies vary almost linearly with the U value with a negative slope in both cases. The DFT
84 (PBE) + U reproduces the activation and reaction energy of the computationally demanding
85 hybrid DFT functional of HSE06 at U values of 3.33 eV and 4.32 eV; respectively. This
86 follows the consensus that there is no universal U value that can produce all experimentally
87 observed parameters such as band gap and lattice constant. The authors' proposed DFT + U
88 methodology to locate transition states encompasses benchmarking the thermodynamic of the
89 reaction against an accurate theoretical framework (i.e., hybrid DFT functional), accurate
90 accounting for f electrons localisation, and rescaling the U value according to the perturbation
91 of geometries between transition state, reactant and product. The authors argued that deploying
92 a single U value along the entire reaction coordinate may induce a significant variation in the
93 overall kinetics of the reaction.

94

95 One of the most prominent catalytic applications of ceria is partial hydrogenation of alkynes
96 cuts into their corresponding alkenes rather than alkanes. Carrasco *et al.* [20]. carried out a
97 combined experimental and DFT study to investigate the selective production of C_2H_4 from
98 hydrogenation of C_2H_2 . Catalytic tests were performed various $\text{H}_2/\text{C}_2\text{H}_2$ inlet ratios in the range

99 of 10-30 within a temperature window of 423 – 623 K and a residence time of 0.12- 1.0 s. The
 100 selectivity toward ethylene attains a value of 80% and remains unchanged even at higher
 101 H_2/C_2H_2 inlet ratios. In order to model the experimentally observed selective formation of
 102 C_2H_4 , Carrasco *et al.* adapted the DFT functional of PBE with the inclusion of a fixed U
 103 parameter at 4.5 eV for Ce atoms. The underlying surface mechanism incorporates four
 104 hydrogen transfer reaction from the $-OH$ site to the free carbon atom in the adsorbed C_2 adduct:
 105



108 The authors attributed the occurrence of partial rather than full hydrogenation rests to lower
 109 activation energy encountered for subsequent hydrogenation leading to gas phase C_2H_4
 110 compared to those leading to with an adsorbed $\beta-C_2H_4$ adduct. Barriers for the first
 111 hydrogenation step in partial and full hydrogenation mechanism were considerably lower than
 112 those of the second step (0.09/0.41 versus 3.65/3.44 eV). We have also observed a similar
 113 trend in our recent study on hydrogenation of acetylene over Mo_2N (111) surface [21]. The
 114 objective of this contribution is to assess the influence of the U parameter on the activation
 115 reaction energies for these four reactions. The underlying aim herein are two-fold; to revisit
 116 conclusions made Capdevila-Cortada *et al.* and to assess the influence of the U parameter on
 117 the thermodynamic and kinetic orderings reported by Carrasco *et al.*
 118

119 Table 1 and Figures 1-4 enlist activation and reaction energies for the two hydrogenation steps
 120 in the partial and full hydrogenation routes for U values between 3.5 – 6.5 eV. Values obtained
 121 with a plain DFT (i.e., $U = 0$) have also been included for comparison. Corresponding values
 122 obtained by Carrasco *et al.* ($U = 4.5$ eV) are highlighted. As displayed in Table 1, activation
 123 energies for the four-hydrogenation reaction increases with the U value. The first
 124 hydrogenation step in the partial hydrogenation route incorrectly incurs a negative value when
 125 the plain PBE functional is applied. The first hydrogenation step in both routes at all U values
 126 require considerably higher energy barriers than the first second step. The activation energy
 127 for the second step in the full hydrogenation route is more sensitive to the U treatment in
 128 reference to the three other reactions. The activation barrier for this step increases from 1.91
 129 eV at $U = 0$ to 3.46 eV at a U value of 4.5 eV. Overall, the variation of the activation energies
 130 in reference to the deployed U value is very significant. The effect is more profound on the

131 reaction rate constants. For instance, at 500 K, a difference of only 0.1 eV in the value of the
132 activation energy changes the reaction rate constant by a factor of ~ 10 . Activation barriers as
133 large as 4.0 eV (~ 92.0 kcal/mol), most likely do not proceed at the relatively low temperature
134 of the catalytic tests (423 – 623 K). Thus, we envisage here that an accurate benchmarking of
135 the exact reaction barriers may stem from surveying via kinetics modelling the kinetic
136 feasibility of the reaction at a given experimental operation conditions.

137

138 Inspection of the U -reaction energy variation displays an analogous thermodynamic sensitivity.
139 Overall, the exothermicity of a given reaction correlates inversely with the U value. Finding
140 the optimum U value for the reaction energy requires benchmarking against very accurate
141 theoretical levels most notably, quantum Monte Carlo (QMC) and the random phase
142 approximation (RPA) or even the relatively more computationally affordable hybrid DFT
143 methods.

144

145

146 Surface-mediated fission of C-H bonds over $\text{CeO}_2(111)$ surface typically occurs above O atoms
147 [20]. On the other hand, we have shown previously that dehydrochlorination reactions
148 preferentially proceeds over O-vacant sites [22]. The effect of the $4f$ electrons is limited to Ce
149 atom, thus, we anticipate results obtained herein to be also applicable to surfaces with oxygen
150 vacant sites.

151

152

153 **4. Conclusions**

154

155 We are now in a position to convey the following concluding remarks and suggestions. As
156 shown in previous studies, the variation in the U value induces a significant effect on computed
157 activation and reaction energies for catalytic CeO_2 -assisted reactions. Higher U values tend to
158 reduce the thermodynamic feasibility of the reaction and increase its activation energy. In
159 addition to comparison with QMC, RPA and hybrid DFT method, detailed kinetic modelling
160 can be utilised as a benchmarking tool in deriving the optimum U value. When feasible,
161 clusters models at more accurate DFT methods (such as B3LYP) may give more accurate
162 kinetics and thermochemical parameters for reaction involving CeO_2 than periodic systems.

163

164

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For Review Only

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173 **References**

174

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Table 1: Variation of activation barriers and reaction energies of acetylene hydrogenation into ethane over the CeO₂(111) surface. Corresponding values by Carrasco *et al.* [20] are highlighted.

| Reaction | Values of U (in eV) | Activation barrier (eV) | Reaction energy (eV) |
|------------------------------------------|-----------------------|-------------------------|----------------------|
| R1 $C_2H_2^*+H^*\rightarrow C_2H_3^*$ | 0 | -0.81 | -1.26 |
| | 3.5 | 0.15 | -1.65 |
| | 4.5 | 0.202 (0.09) | -1.42 (-1.45) |
| | 5.5 | 0.205 | -1.21 |
| | 6.5 | 0.296 | -0.99 |
| R2 $C_2H_3^*+H^*\rightarrow C_2H_4^*$ | 0 | 3.24 | 1.71 |
| | 3.5 | 3.50 | 1.95 |
| | 4.5 | 3.77 (3.65) | 2.17 (2.13) |
| | 5.5 | 3.99 | 2.38 |
| | 6.5 | 4.20 | 2.59 |
| R3 $C_2H_4^*+H^*\rightarrow C_2H_5^*$ | 0 | 0.25 | -0.63 |
| | 3.5 | 0.30 | -0.59 |
| | 4.5 | 0.39 (0.41) | -0.99 (-1.03) |
| | 5.5 | 0.50 | -0.77 |
| | 6.5 | 0.66 | -0.62 |
| R4 $C_2H_5^*+H^*\rightarrow C_2H_6^*$ | 0 | 1.91 | 0.46 |
| | 3.5 | 3.00 | 0.88 |
| | 4.5 | 3.46 (3.44) | 1.32 (1.20) |
| | 5.5 | 3.89 | 1.75 |
| | 6.5 | 4.32 | 2.17 |

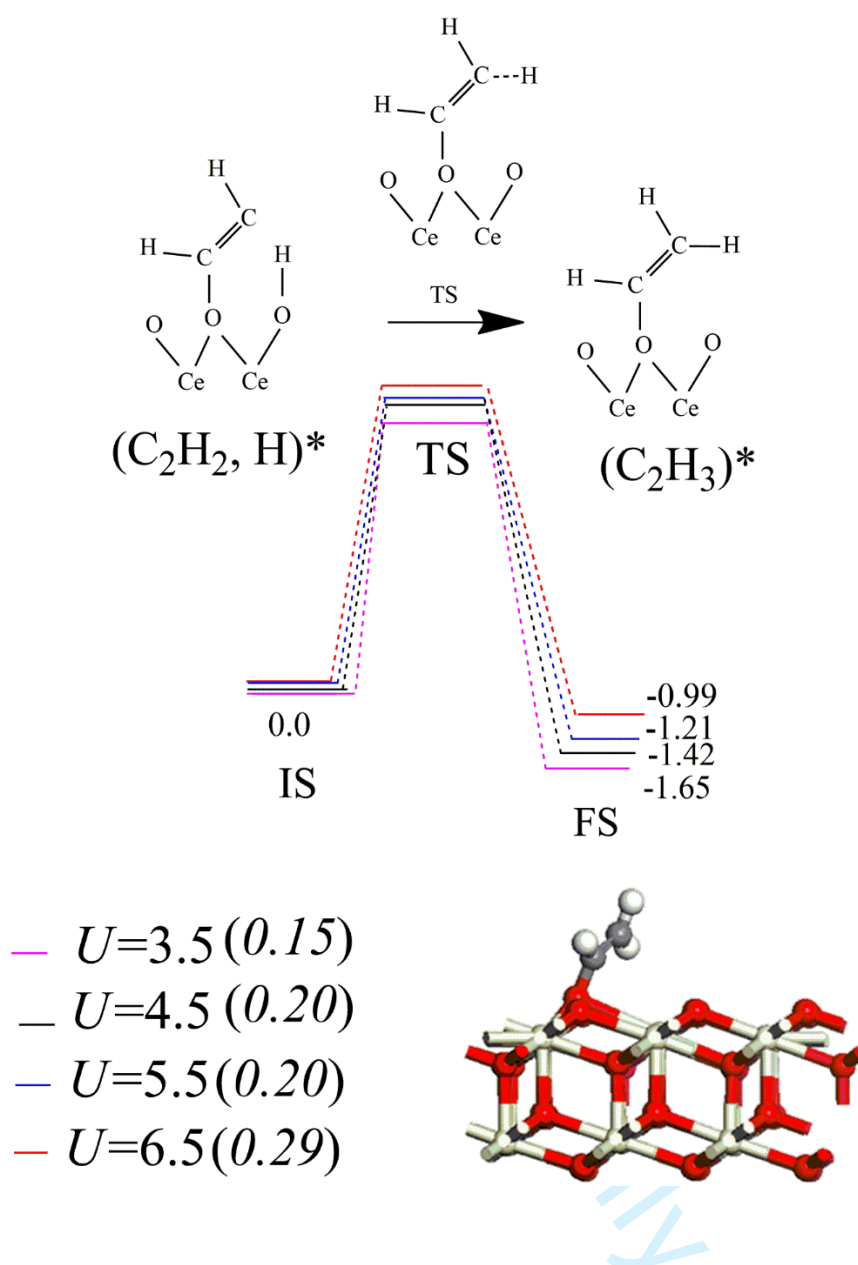


Figure 1: Energy profile for the first hydrogenation step in the partial hydrogenation route of acetylene over the CeO₂(111) surface at different U values. Values of activation barriers (in italic font) and reaction energies are in eV with respect to the initial reactant. Red, cream, gray, and white stand for Oxygen, Cerium, Carbon, and Hydrogen, respectively (this colour code applies in Figures 2-4 also). IS, TS and FS denote initial state, transition state, and final state, respectively. U values are in eV.

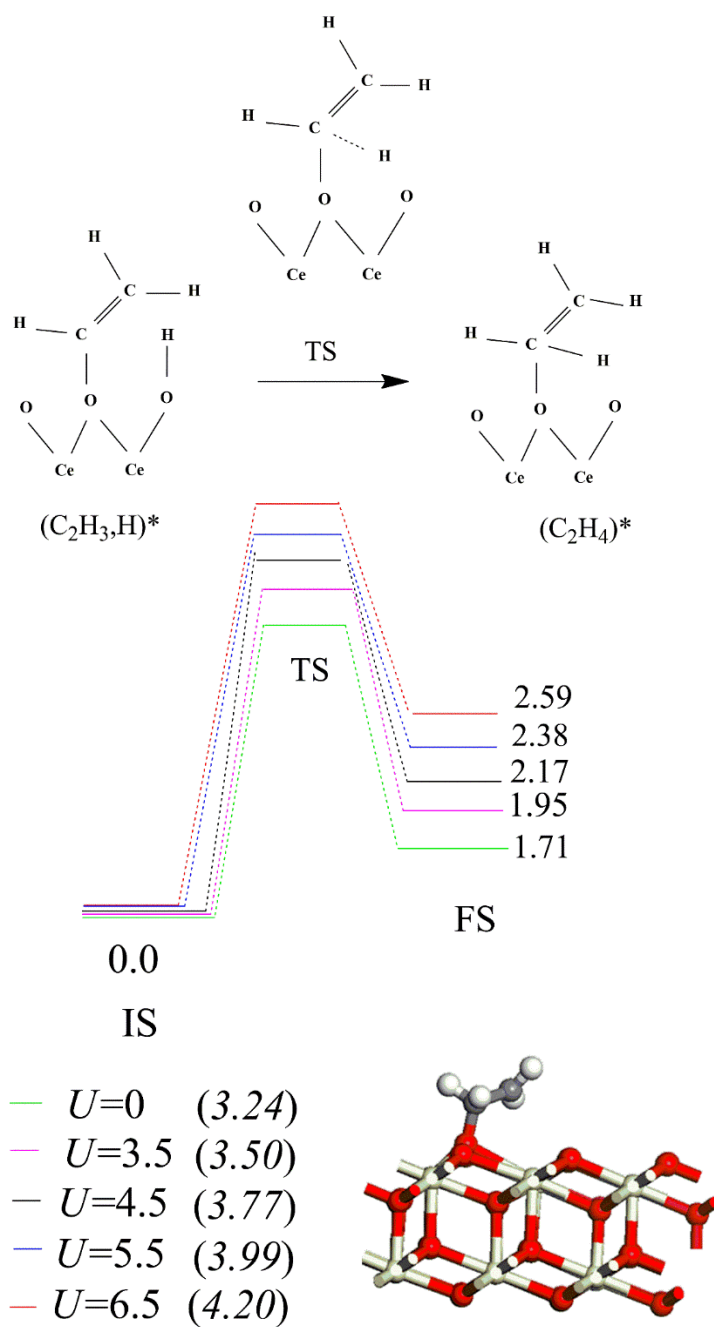


Figure 2: Energy profile for the second hydrogenation step in the partial hydrogenation route of acetylene over the $CeO_2(111)$ surface at different U values. Values of activation barriers (in italic font) and reaction energies are in eV, with respect to the initial reactant.

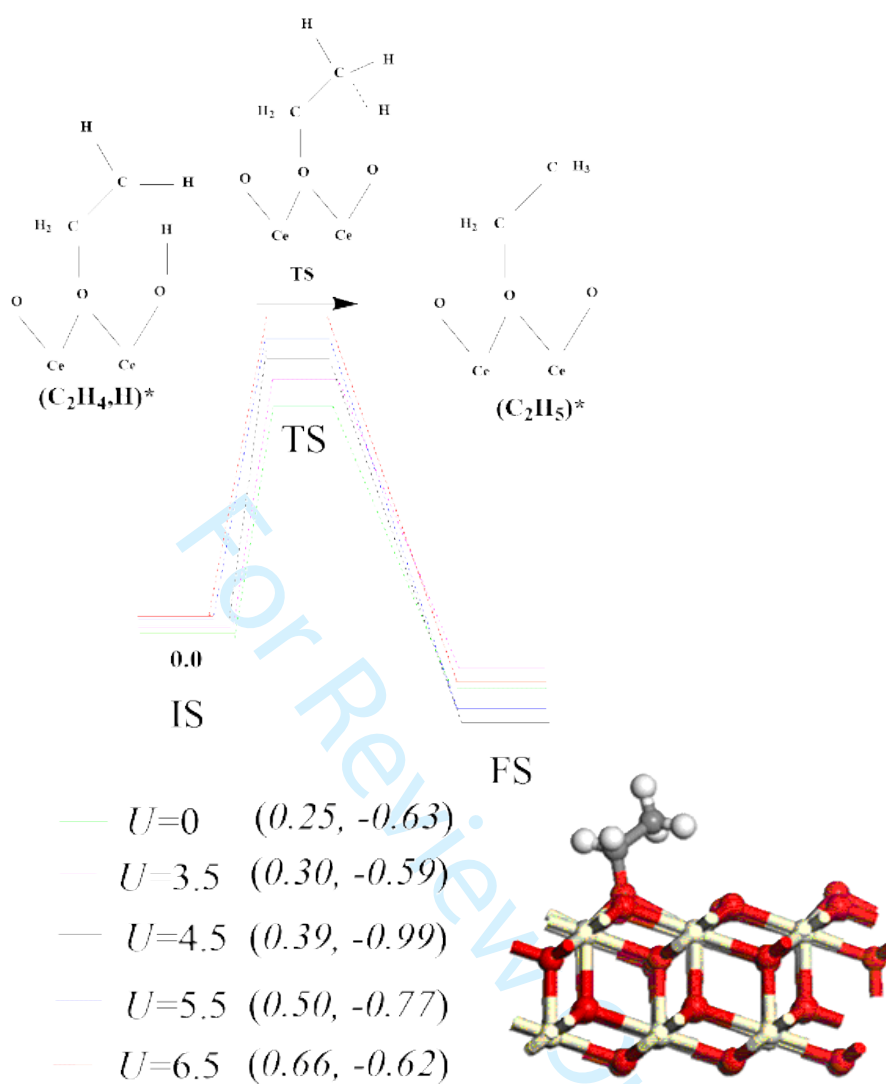


Figure 3: Energy profile for the first hydrogenation step in the full hydrogenation route of acetylene over the $\text{CeO}_2(111)$ surface at different U values. Values of activation barriers (in the italic font) and reaction energies are in eV, with respect to the initial reactant.

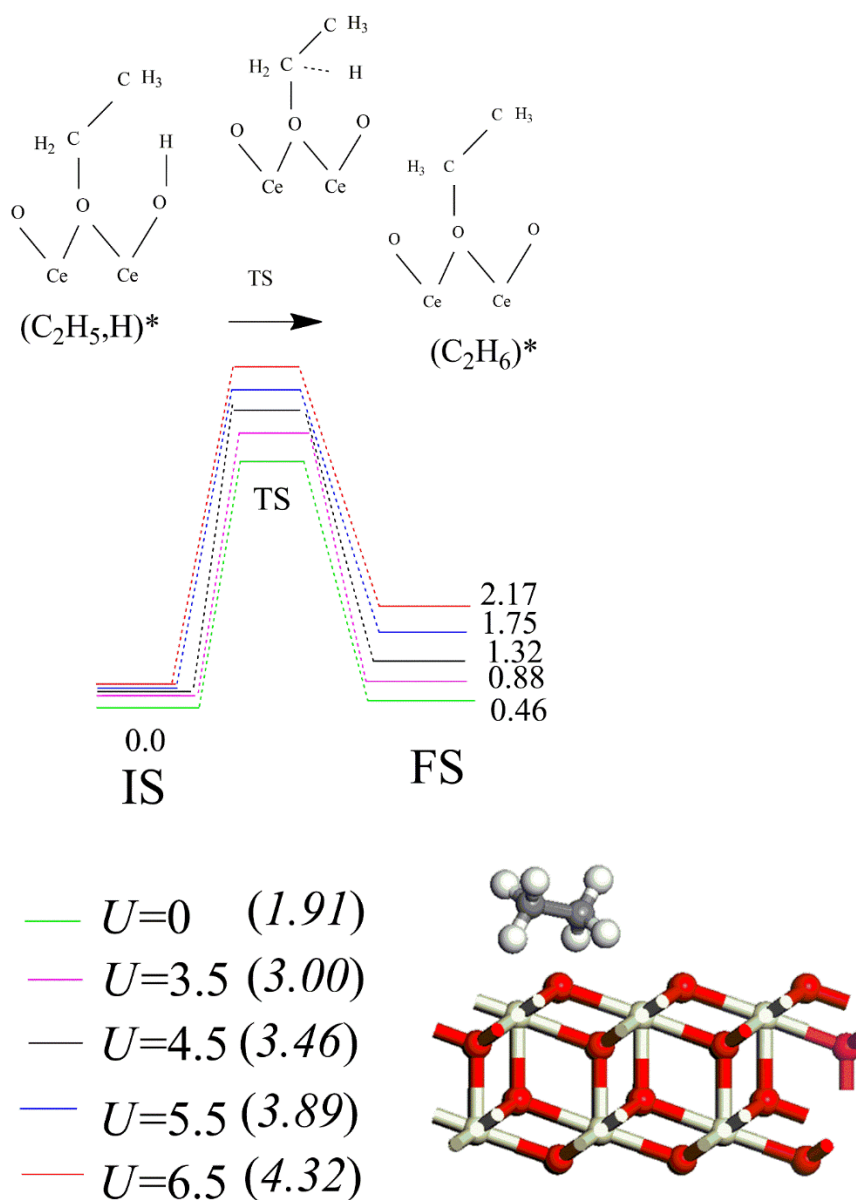


Figure 4: Energy profile for the second hydrogenation step in the full hydrogenation route of acetylene over the $CeO_2(111)$ surface at different U values. Values of activation barriers (in italic font) and reaction energies are in eV with respect to the initial reactant.