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Selective hydrogenation of acetylene over Cu(211), Ag(211) and Au(211): Horiuti–Polanyi mechanism vs. non-Horiuti–Polanyi mechanism†

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Two hydrogenation mechanisms, namely the Horiuti–Polanyi and non-Horiuti–Polanyi mechanisms, are examined and compared for acetylene hydrogenation to ethylene over Cu(211), Ag(211) and Au(211) using density functional theory (DFT) calculations. In the Horiuti–Polanyi mechanism, hydrogen molecules dissociate first followed by the sequential addition of hydrogen atoms to the hydrocarbon, whilst in the non-Horiuti–Polanyi mechanism, hydrogen molecules react with the hydrocarbon directly. It is found that the Horiuti–Polanyi mechanism is favoured on Cu(211) for the hydrogenation reactions of acetylene to ethylene, whilst the non-Horiuti–Polanyi mechanism is favoured for the reactions over Ag(211). In contrast, on Au(211) the hydrogenation of C₂H₂ and C₂H₃ follows the Horiuti–Polanyi mechanism, but the hydrogenation of C₂H₄ follows the non-Horiuti–Polanyi mechanism. Further analyses suggest that the non-Horiuti–Polanyi mechanism is favoured when the reactants weakly adsorb while strong adsorption gives rise to the Horiuti–Polanyi mechanism, which is consistent with the observations reported in our previous work. From the energy profiles obtained, the activity and selectivity of the hydrogenation reactions are also quantitatively estimated and compared.

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1. Introduction

The process of molecular hydrogen dissociation followed by the sequential addition of hydrogen atoms to a wide range of unsaturated compounds, including aldehydes, ketones, alkenes *etc.*, is widely recognised as the Horiuti–Polanyi mechanism. It has been utilized for the explanation of heterogeneous hydrogenation reactions since it was first proposed in the 1930s.^{1–3} However, our recent work, investigating the hydrogenation of the simplest α,β -unsaturated aldehyde, acrolein, provided strong evidence that, instead of atomic hydrogen, molecular hydrogen (H₂) might be the reacting species in hydrogenation reactions occurring over Au surfaces with different structures, which gives rise to a non-Horiuti–Polanyi mechanism.⁴ Furthermore, two pathways, *i.e.* Horiuti–Polanyi and non-Horiuti–Polanyi hydrogenation pathways, were examined by comparing the energies of the rate determining transition states in each pathway.⁴

In addition to the selective hydrogenation of aldehydes and ketones, another large group of hydrogenation reactions in the industry is the selective hydrogenation of alkynes, and the catalysts used in the industry mainly consist of Pd alloyed with other metals. Although group 11 metals have commonly been used as promoters for Pd,^{5–20} they were found to be active and highly selective towards alkyne hydrogenation while in supported nano-particle formulations. Recent experimental studies on propyne hydrogenation over Cu catalysts showed that the selectivity to propene formation is rather high under optimal reaction conditions, but the activity is relatively low: the conversion is as low as ~40% at temperatures up to 423 K.^{21,22} Further density functional theory (DFT) calculations showed that the dissociation of molecular hydrogen on Cu(111) is marginally endothermic (0.16 eV) and is hindered by a large barrier of 0.83 eV, which is higher than those of the subsequent hydrogenation steps. The hydrogenation of acetylene over Ag catalysts was investigated by Sárkány and Révay.²³ They found that Ag catalysts possess low activity for acetylene hydrogenation, but 100% semi-hydrogenation selectivity to ethylene at low temperatures. Alkyne hydrogenation using gold as catalysts has been studied by many groups,^{17,22,24–33} and was firstly reported by Jia *et al.* Therein, it was reported that the selective hydrogenation of acetylene over Au/Al₂O₃ would give 100% selectivity to ethylene in the temperature range between 313 and 523 K. Moreover, the hydrogenation of ethylene on the catalyst occurred

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only at much higher temperatures above 573 K.²⁴ One can see from the above results that supported Cu, Ag and Au catalysts all show high selectivity but lower activity than those conventional heterogeneous PGM catalysts, *e.g.* Pd and Pt. Recent studies by Vilé *et al.*, combining experiments and theoretical calculations, found that the hydrogenation of propyne over Ag also follows the non-Horiuti–Polanyi mechanism.³⁴ Therefore, it is of interest to extend our findings from the hydrogenation of α,β -unsaturated aldehydes to the hydrogenation of other unsaturated hydrocarbon and from the effect of surface structures to the effect of using different metal catalysts, in order to obtain a more complete picture of the mechanisms involved and, more importantly, the trends of the activity and selectivity of heterogeneous hydrogenation reactions.

In the current work, the adsorption of the reactants, *i.e.* C₂H₂ and H₂, have been compared on Cu(211), Ag(211) and Au(211), which are typical surface terminations used to represent the active sites of these metals with low coordination number. The Horiuti–Polanyi and non-Horiuti–Polanyi hydrogenation pathways have also been examined in detail for the hydrogenation of C₂H₂, C₂H₃ and C₂H₄ over these surfaces. In order to obtain the corresponding activity and selectivity of C₂H₂ hydrogenation over each surface, the energy profiles of C₂H₂ hydrogenation were obtained by combining the favoured Horiuti–Polanyi/non-Horiuti–Polanyi hydrogenation pathways.

2. Computational details

DFT calculations were performed using the Vienna *ab initio* simulation package (VASP) in slab models.^{35–38} The exchange–correlation functional of PW91 was used to calculate the electronic structure.³⁹ The projector augmented wave (PAW) method was employed to describe the interaction between the atomic cores and electrons.^{40,41} For Cu(211), Ag(211) and Au(211), 12-layer 1 × 4 unit cells with the top 6 layers relaxed during optimization were used to model the adsorption and reaction processes. A 4 × 2 × 1 *k*-point sampling in the surface Brillouin zone was used for these surfaces. The vacuum was set to be more than 12 Å. A cut-off energy of 500 eV and a force threshold on each relaxed atoms below 0.05 eV Å^{−1} were used in the current work. The transition states were located with a constrained minimization method.^{42–44} The adsorption/binding energies ($E_{\text{ad/bind}}$) are defined as:

$$E_{\text{ad/bind}} = E_{\text{total}} - (E_{\text{g}} + E_{\text{slab}}) \quad (1)$$

Table 1 Adsorption/binding energies (eV) of H, C₂H₂, C₂H₃ and C₂H₄ on Cu(211), Ag(211) and Au(211). The adsorption/binding energies are calculated with eqn (1), and those of H are with respect to the total energy of gaseous 1/2H₂. All the energies are ZPE corrected

	H	C ₂ H ₂	C ₂ H ₃	C ₂ H ₄
Cu(211)	−0.24	−1.36	−2.44	−0.54
Ag(211)	0.19	0.06	−1.74	−0.21
Au(211)	0.04	−0.56	−2.00	−0.35

Table 2 Calculated reaction barriers (eV) of hydrogen dissociation ($E_{\text{a,D}}$), hydrogenation by atomic hydrogen ($E_{\text{a,A}}$) and molecular hydrogen ($E_{\text{a,M}}$) of C₂H₂, C₂H₃ and C₂H₄ on Cu(211), Ag(211) and Au(211). These barriers are with respect to the energies of the adsorbed C₂ species and gaseous H₂ or 1/2H₂. All the energies are ZPE corrected

		Cu(211)	Ag(211)	Au(211)
C ₂ H ₂	$E_{\text{a,D}}$	0.38	1.16	0.56
	$E_{\text{a,A}}$	0.61	0.80	0.52
	$E_{\text{a,M}}$	1.09	0.45	0.94
C ₂ H ₃	$E_{\text{a,A}}$	0.48	1.00	0.66
	$E_{\text{a,M}}$	0.48	0.87	0.76
C ₂ H ₄	$E_{\text{a,A}}$	0.15	0.76	0.66
	$E_{\text{a,M}}$	0.90	0.87	0.72

where E_{total} is the energy of the system after adsorption, E_{g} is the energy of the gas phase species and E_{slab} is the energy of the slab. The temperature was set to 523 K, which is commonly used in the hydrogenation of acetylene with Cu, Ag and Au catalysts experimentally, while obtaining the free energies.^{17,21,22,24,27,30,31,45,46}

3. Results and discussion

The adsorption of H₂ and C₂H₂ was investigated initially and the adsorption energies of H and C₂H₂ on the Cu(211), Ag(211) and Au(211) surfaces are listed in Table 1. It should be noted that the adsorption energies of H are referenced with the total energy of gaseous 1/2H₂. We have calculated the energies of all the possible adsorption and transition state configurations at the possible surface active sites, the corresponding adsorption energies and reaction barriers are listed in the ESI,[†] and those presented in the main text are the lowest ones. Hence, the dissociative adsorption energies of H₂ on Cu(211), Ag(211) and Au(211) are −0.48 eV, 0.38 eV and 0.08 eV,

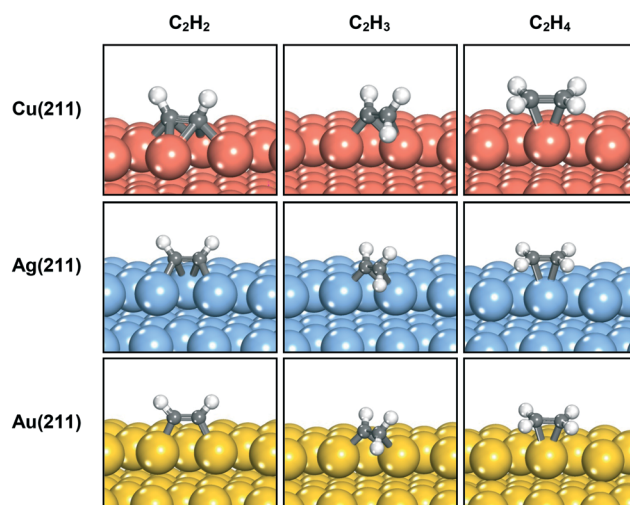


Fig. 1 Adsorption configurations of C₂H₂, C₂H₃ and C₂H₄ on Cu(211), Ag(211) and Au(211). The red, blue, yellow, grey and white balls denote the copper, silver, gold, carbon and hydrogen atoms, respectively. This notation is used throughout this paper.



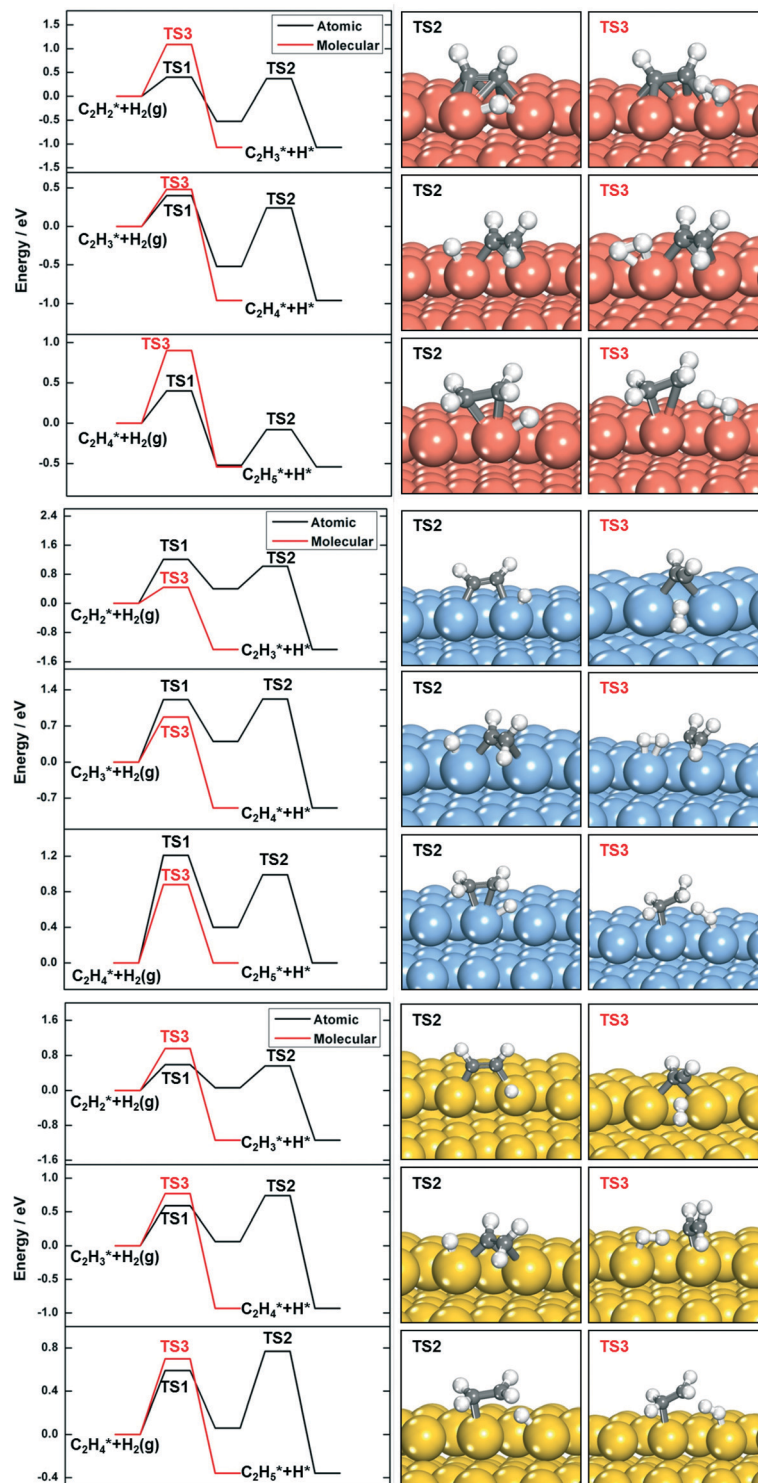


Fig. 2 Energy profiles of the hydrogenation of C_2H_2 (first panel), C_2H_3 (second panel) and C_2H_4 (third panel) by atomic and molecular hydrogen on Cu(211), Ag(211) and Au(211). (g) and * indicate the gaseous and adsorption states, respectively. TS1, TS2 and TS3 are the transition states of hydrogen dissociation, hydrogenation by atomic and molecular hydrogen, respectively. Also shown are the corresponding transition state structures of the hydrogenation by atomic (TS2) and molecular (TS3) hydrogen.

respectively, and the dissociation barriers with respect to the gaseous total energy of H_2 on Cu(211), Ag(211) and Au(211) were calculated to be 0.38 eV, 1.16 eV and 0.56 eV, respectively, as listed in Table 2.

Using different methods (mobile, immobile and collision theory models), we found recently that the rate of adsorption/desorption step is strongly affected by the entropic factor, and real adsorption transition states generally locate between



those obtained with mobile and immobile models.⁴⁷ In the current work, we use the immobile model to estimate the upper limit of the adsorption free energy barriers by assuming that the adsorbate loses all the entropy at the adsorption transition state. Therefore, the free energy barriers of the adsorption processes are close to TS where T and S are the temperature and the entropy of gaseous molecules, respectively. This approach has been widely used in our previous work and we found it is effective to estimate the adsorption free energy barriers.^{19,20,33,48–54} However, we will show later that the approach used to estimate the adsorption/desorption free energy barriers would not vary the conclusions made in our work. Due to the entropic effects, the effective dissociative adsorption free energy barriers of H_2 on Cu(211), Ag(211) and Au(211) surfaces at 523 K are estimated to be 1.09 eV, 1.87 eV and 1.27 eV, respectively, using the entropy data reported before.⁵⁵ Furthermore, the adsorption free energy barriers of C_2H_2 onto the catalyst surfaces can be estimated to be 1.09 eV at 523 K. Considering that the adsorption energies of C_2H_2 on these surfaces are also higher than those of H_2 on all the surfaces studied (see Table 1), we find that, at the initial stage of the reaction, it is more difficult for H_2 adsorption onto the surfaces than for C_2H_2 .

The adsorption/binding energies of C_2H_3 and C_2H_4 on the surfaces calculated are also listed in Table 1 and the corresponding adsorption configurations on the surfaces are shown in Fig. 1. It is clear that the adsorption geometries of C_2H_3 and C_2H_4 on all the three surfaces are almost identical, *i.e.* C_2H_3 adsorbs at the bridge sites along the step edge and C_2H_4 adsorbs at the step edges in a π -bonded configuration. All the transition states of the elementary reactions, *i.e.* the dissociation of H_2 molecules, hydrogenation of C_2 species with atomic and molecular hydrogen species, are located on each surface and the reaction barriers are listed in Table 2. The energy profiles of the hydrogenation pathways of C_2H_2 , C_2H_3 and C_2H_4 by molecular and atomic hydrogen on Cu(211), Ag(211) and Au(211) are shown in Fig. 2, along with the transition state structures of hydrogenation reactions. From these results, the following trends are readily obtained:

(i) On Cu(211), the hydrogenation of all the C_2 species follow the Horiuti–Polanyi mechanism, whilst on Ag(211) the non-Horiuti–Polanyi mechanism is favoured for all the hydrogenation pathways.

(ii) On Au(211), the hydrogenation of C_2H_2 and C_2H_3 follow the Horiuti–Polanyi mechanism and the hydrogenation of C_2H_4 follows the non-Horiuti–Polanyi mechanism.

Further analysis is carried out by plotting the transition state energies of the rate determining steps in each pathway, with respect to the corresponding gas phase energies of $C_2H_2 + H_2$, $C_2H_3 + H_2$ and $C_2H_4 + H_2$ (defined as E_{TS-gas}), as a function of the adsorption/binding energies of $C_2H_2 + 2H$, $C_2H_3 + 2H$ and $C_2H_4 + 2H$ (defined as E_{ad}), respectively, over each surface. In all cases, a linear relationship is obtained (see Fig. 3). Importantly, it is clear that the non-Horiuti–Polanyi mechanism is favoured when the reactants weakly adsorb whilst the strong adsorption leads to the Horiuti–Polanyi

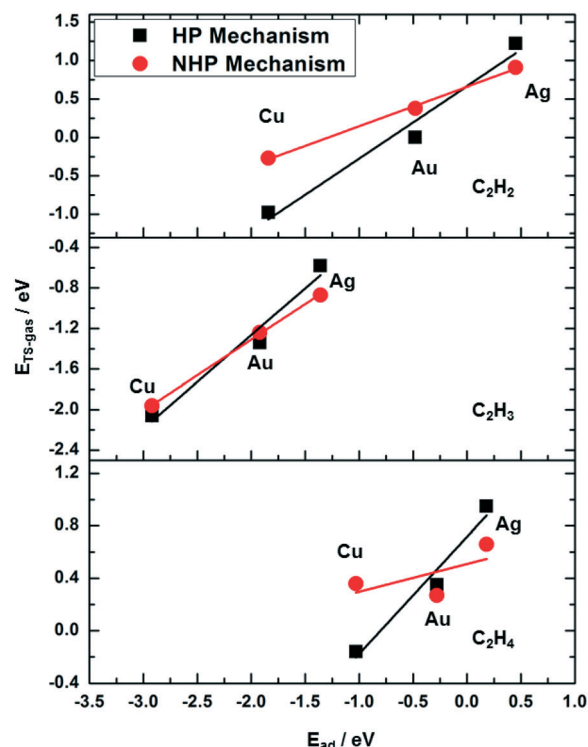


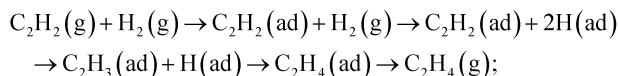
Fig. 3 The relationship between the transition state energies of the rate determining steps in each pathway referenced to the gas phase $C_2H_2 + H_2$, $C_2H_3 + H_2$ or $C_2H_4 + H_2$ energy (E_{TS-gas}) and the adsorption or binding energies of $C_2H_2 + 2H$, $C_2H_3 + 2H$ or $C_2H_4 + 2H$ (E_{ad}) investigated in this work. HP mechanism and NHP mechanism are the Horiuti–Polanyi mechanism and non-Horiuti–Polanyi mechanism, respectively.

mechanism being favoured. This is consistent with the results reported in our previous work,⁴ indicating that the trend of different hydrogenation mechanisms observed for the hydrogenation of α,β -unsaturated aldehydes can also be applied to understand the hydrogenation reactions of unsaturated hydrocarbons.

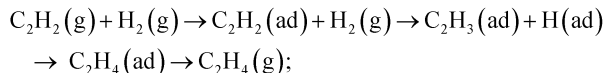
From the elementary steps obtained, the activity and selectivity of ethylene formation from acetylene hydrogenation on Cu(211), Ag(211) and Au(211) have been determined. The energy profiles derived for the hydrogenation of acetylene to ethylene are shown in Fig. 4. It should be noted that the Horiuti–Polanyi pathway of C_2H_3 hydrogenation is hindered by the high dissociation barrier of H_2 over Ag(211), as one can see from Fig. 2. However, in the whole process of C_2H_2 hydrogenation to C_2H_4 over Ag(211), the first hydrogenation step, *i.e.* C_2H_2 hydrogenation, follows the non-Horiuti–Polanyi mechanism, and the surface contains adsorbed hydrogen atoms for the subsequent reaction to C_2H_3 . Interestingly, the subsequent hydrogenation of C_2H_3 with this surface adsorbed hydrogen atom is found to be favoured over the corresponding hydrogenation with molecular hydrogen, and a similar result was also observed in the recent work reported by Vilé *et al.*³⁴ Therefore, the process of the hydrogenation of C_2H_2 to C_2H_4 over these surfaces can be written as:



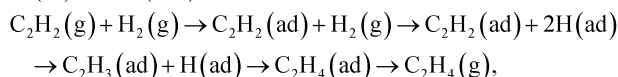
(i) on Cu(211):



(ii) on Ag(211):



(iii) on Au(211):



where (g) and (ad) represent the gaseous and adsorption states, respectively.

On Cu(211), Ag(211) and Au(211), the free energy of gaseous $\text{C}_2\text{H}_2 + \text{H}_2$, -1.80 eV with respect to their gaseous total energy, can be considered to be the energy of the initial state on all surfaces. Therefore, the effective barriers (E_a^{eff}) of C_2H_2 hydrogenation to C_2H_4 on Cu(211), Ag(211) and Au(211) can be estimated as 1.09 eV, 2.23 eV and 1.74 eV, respectively, using the approach introduced previously,^{19,20,51,52,56} and the dissociative adsorption of H_2 or the hydrogenation of C_2H_2 to C_2H_3 is rate-determining in the whole process of acetylene hydrogenation over all the surfaces studied. Considering that the adsorption energies of C_2H_2 over Cu(211), Ag(211) and Au(211) surfaces are -1.36 eV, 0.06 eV, -0.56 eV, respectively, it is observed that the activity of C_2H_2 hydrogenation in-

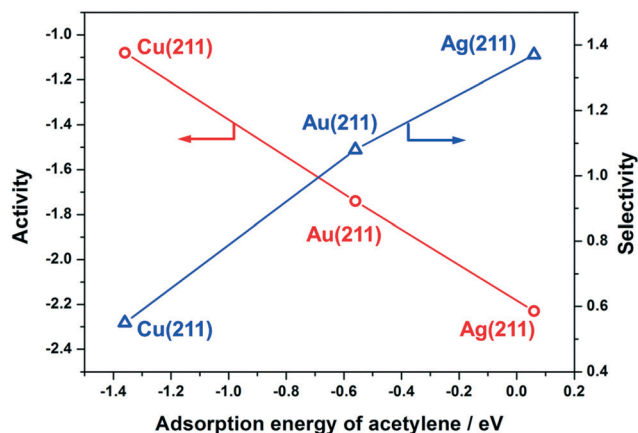


Fig. 5 Activity and selectivity of Cu(211), Ag(211) and Au(211) for the hydrogenation of acetylene to ethylene plotted as a function of the adsorption energy of acetylene. The activity and selectivity is measured by the values of $-E_a^{\text{eff}}$ and ΔE_a , respectively.

creases with the stronger C_2H_2 adsorption, indicating that the activity of these surfaces lies on the weak adsorption side of the volcano curve of acetylene hydrogenation.^{52,57} The selectivity, which is defined as ΔE_a , can be estimated from the difference between the hydrogenation barrier of C_2H_4 and the absolute value of the C_2H_4 adsorption energy on each surface, i.e. $\Delta E_a = E_{a,\text{hydr}} - |E_{\text{ad}}|$. Therefore, the higher the value of ΔE_a is, the higher the selectivity of ethylene will be. As mentioned above, the hydrogenation of ethylene follows the Horiuti–Polanyi mechanism over Cu(211), whilst on Ag(211) and Au(211) the non-Horiuti–Polanyi mechanism is followed. Therefore, the hydrogenation barriers of ethylene are strongly dependent on temperature due to the entropic factor. At 523 K, the ΔE_a values on Cu(211), Ag(211) and Au(211) are obtained to be 0.55 eV, 1.37 eV and 1.08 eV, respectively.

Fig. 5 shows the values of $-E_a^{\text{eff}}$, which could be used to measure the catalytic activity, and ΔE_a as a function of the adsorption energy of acetylene over the surfaces studied. From Fig. 5 the Cu(211) surface is found to have the highest activity but lowest selectivity to ethylene, whereas Ag(211) shows the lowest activity, but the highest selectivity. The activity and selectivity of Au(211) are between the values of Ag and Cu. Importantly, one can see that these trends would not be changed with the approach we used to estimate the adsorption free energy barriers as mentioned above. It should be mentioned that these results are consistent with the trend observed experimentally, e.g. at 523 K, the hydrogenation of alkynes gives 100% conversion and $<80\%$ selectivity to alkenes on Cu catalyst, whilst Au catalyst gives $\sim 50\%$ conversion and $\sim 90\%$ selectivity for the hydrogenation.^{21,27}

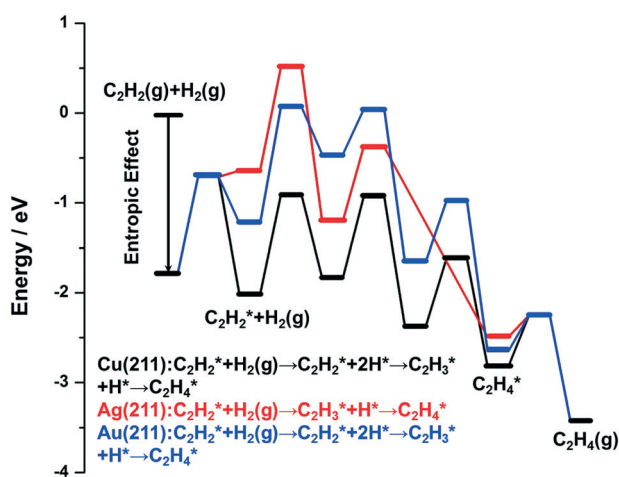


Fig. 4 Energy profiles of acetylene hydrogenation over Cu(211), Ag(211) and Au(211). (g) and * indicate the gaseous and adsorption states, respectively. The relevant elementary steps considered are also shown. Entropic effects are considered for the energy of gaseous $\text{C}_2\text{H}_2 + \text{H}_2$ and C_2H_4 . The adsorption/desorption transition state free energies are estimated with the corresponding total energies.

4. Conclusions

The Horiuti–Polanyi and non-Horiuti–Polanyi mechanisms have been examined with respect to the hydrogenation of acetylene on Cu(211), Ag(211) and Au(211) surfaces, in order to further investigate the universality of the trends of the



Horiuti–Polanyi and non-Horiuti–Polanyi mechanisms reported recently for the hydrogenation of carbonyl containing molecules. Herein, on Cu(211), the hydrogenation of C₂ species was found to follow the Horiuti–Polanyi mechanism, whilst on Ag(211) the non-Horiuti–Polanyi mechanism is preferred for all the hydrogenation pathways of C₂ species. However, when combining all the hydrogenation pathways together, we found that the hydrogenation of C₂H₃ with atomic hydrogen is preferred over Ag(211). On Au(211), the hydrogenation of C₂H₂ and C₂H₃ follows the Horiuti–Polanyi mechanism and the hydrogenation of C₂H₄ follows the non-Horiuti–Polanyi mechanism. Therefore, it can be concluded more generally that the whole hydrogenation processes are a combination of the two mechanisms. After quantitatively estimating the activity and selectivity of acetylene hydrogenation from the energy profiles of acetylene hydrogenation on all the surfaces, it was observed that the Cu(211) surface possesses the highest activity but lowest selectivity and Ag(211) shows the lowest activity but highest selectivity. The activity and selectivity of Au(211) is found to lie between the values found for Ag and Cu. The current work provides an extended understanding on the mechanisms of hydrocarbon hydrogenation over noble transition metals surfaces, and further strengthens the importance of considering both mechanistic pathways in the study of hydrogenation reactions.

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