DFT and Microkinetic Study of Acetylene Hydrogenation and Decomposition over the (111) surfaces of Pd, M and PdM alloys (M=Cu, Ag, Au)

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Adsorption

1. CHCH

On Pd(111), acetylene preferentially adsorbs at the 3-fold hollow sites, with the adsorption energy of $-2.02$ eV, consistent with previous study¹. On Ag(111) and Au(111), the adsorption energy of acetylene decreases to $-0.04$ eV on Ag(111) and $-0.17$ eV on Au(111). However, on Cu(111) surface it prefers to adsorb at the “4-fold diagonal hollow” site with an adsorption energy of $-1.14$ eV, which agrees with the experimental and theoretical results reported in literature²³. When alloyed with Pd, the adsorption of acetylene on the three coin metal alloy surface increases, being $-1.42$eV on PdCu(111), $-1.22$eV on PdAg(111) and $-1.14$eV on PdAu(111). These values are close to the result on Cu(111). The decreasing order of adsorption energy from PdCu(111), PdAg(111) to PdAu(111) may be due to the variation of the lattice constants which increase from PdCu (3.81 Å) to PdAu (4.05 Å). It is noted that the adsorption configuration of acetylene on these alloy surfaces is similar to that on Pd(111) and the C atoms bind to the surface Pd atoms.

2. CHCH₂

The intermediate vinyl CHCH₂ always has larger adsorption energies than C₂H₂. The favorite adsorption site over M(111) (M=Pd, Cu, Ag, Au) is the 3-fold hollow
with the adsorption energies of \(-2.84\) eV, \(-1.89\) eV, \(-1.28\) eV and \(-1.64\) eV over Pd(111), Cu(111), Ag(111) and Au(111). Introduction of Pd into Cu, Ag and Au surfaces also enhances the substrate-adsorbate interaction, as evidenced by the decreased adsorption energies from \(-2.04\) to \(-2.31\) eV on PdM(111), compared to \(-1.28\) to \(-1.89\) eV on M(111). The adsorption energies for vinyl are lowered to \(-2.31\) eV, \(-2.04\) eV and \(-2.05\) eV for PdCu(111), PdAg(111) and PdAu(111). Structurally the CH group in vinyl shifts from a bridging site on M(111) to an atop Pd site on PdM(111).

3. CH₂CH₂

Ethylene adsorbs most favorably in the di-σ adsorption mode over Pd(111). The adsorption energy is calculated to be \(-0.93\) eV, which is consistent with previous study\(^1\). On the three coin metals the adsorption geometry of ethylene becomes π mode and the adsorption energies are \(-0.17\) eV, \(-0.05\) eV and \(-0.09\) eV on the Cu, Ag and Au surfaces respectively. as on Pd(111), ethylene also exhibits the di-σ mode in which the two C atoms interact with the two adjacent bridging Pd atoms on the PdM(111) surfaces. The adsorption energies are 0.25 eV higher than \(-0.93\) eV on Pd(111).

4. CH₂CH₃

Ethyl adsorbs on the all surfaces with its CH₂ group bound an atop metal atom. On M(111) the adsorption energies range from \(-0.77\) eV on Ag(111) to \(-1.72\) eV on Pd(111). On the PdM(111), it prefers to adsorb atop Pd rather than atop M, and the adsorption energies are about \(-1.5\)eV.

5. CH₃CH₃

Ethane is a saturated hydrocarbon molecule and it binds to the substrate through weak van der Waals interactions only. The predicted adsorption energies of ethane over the seven surfaces are less than \(-0.15\)eV.

6. CHCH₃

Ethylidene preferentially sits at the bridge site on Pd(111) with an adsorption energy of \(-3.76\) eV. On the (111) surfaces of Cu, Ag and Au, the binding energies of ethylidene are reduced to \(-2.64\) eV, \(-1.77\) eV and \(-2.41\) eV, respectively. The
preferential site is also the bridge site on the coin metal M surfaces. On all the PdM(111), the binding energy of CHCH$_3$ increases by about 0.4 eV in going from the Pd(111) (−3.76 eV) to ~ −3.3eV on over the PdM(111). The favored sites are the bridge site formed by two Pd atoms.

7. CH$_x$(X=0~3)

In all the favorable adsorption sites, the atom C bonding to the surfaces fulfills sp$^3$ configuration. Thus, CH$_3$ sits at a top site favorably; CH$_2$ occupies a bridge site and CH prefers to adsorb at a 3-fold fcc hollow site. Atomic carbon prefers to adsorb on the 3-fold hollow site with strong binding to all surfaces. It is more strongly bound to Pd than to M. The calculated adsorption energy over Pd(111) is −6.93 eV, whereas the values are −4.82eV, −3.33eV and −4.51eV on Cu(111), Ag(111) and Au(111). On PdM(111) facets, atomic carbon adsorbs at the 3-fold hollow site consisting of two Pd atoms and one M atom. The calculated adsorption energies are −5.95 eV, −5.89 eV and −6.12eV on the (111) surfaces of PdCu, PdAg and PdAu, respectively, which are about 1.0 eV higher than that on Pd(111).

The adsorption energies depend on the coordination number of CH$_x$ species with the substrate. Hence, following the atomic carbon, the adsorption energies of CH is the second largest, and CH$_3$ has the smallest one. As expected, the CH$_x$ intermediates are more strongly bound to Pd than to M sites.

9. CCH$_x$(X=1~3)

All the intermediates CCH$_x$ (x=1~3) prefer to adsorb at 3-fold fcc hollow site. The C-C bond axis of adsorbed CCH and CCH$_3$ is perpendicular to the surface, whereas that of CCH$_2$ tilts about 80 degrees to the surface with CH$_2$ weakly interacting with the nearest surface Pd atom.
Figure S1 (a) FCC structures of PdM

(b) Top view structures for the (111) surfaces of PdCu, PdAg and PdAu.

Figure S2 Relationship between CHCH adsorption energy and d-band center.
Figure S3 Adsorption energies of all species on PdM(111) plotted against that on Pd(111) and M(111) (M=Cu, Ag, Au).

Figure S4 Adsorption energies of CH\textsubscript{x} intermediates (squares: x=1; circles: x=2; triangles: x=3) plotted against adsorption energies of atom C.
Figure S5 Adsorption energies of CCH\textsubscript{x} reactants plotted against adsorption energies of atom C.

Figure S6 Adsorption energies of C\textsubscript{2}H\textsubscript{y} intermediates plotted against adsorption energies of atom C.
Figure S7 Transition states structures of CHCH hydrogenation to CH$_3$CH$_3$ over Pd(111), M(111) and PdM(11) (M=Cu, Ag, Au).
Table S1 Optimized structural parameters (pm) for the initial state (IS), transition state (TS), and final state (FS) of the CHCH→CH₃CH₃ reactions on Pd(111) and PdM(111) (M=Cu, Ag, Au) surfaces.

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<td>143</td>
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Table S2 The reaction energies (eV) of CHCH→CH₃CH₃ over Pd(111), M(111) and PdM(111) (M=Cu, Ag, Au) surfaces.

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<th>PdCu</th>
<th>PdAg</th>
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<td>CH₂CH₂+H→CH₂CH</td>
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<td>-0.55</td>
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<td>CH₂CH₃+H→CH₃CH</td>
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3
Figure S8 Reaction rates predicted by the microkinetic simulations of H\textsubscript{2}, CHCH and CH\textsubscript{2}CH\textsubscript{2} conversion over Cu(111), Ag(111) and Au(111).
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Table S4 Elementary reaction net rates (s$^{-1}$) over Pd(111) and PdM(111) at 450K.

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<th>Reaction</th>
<th>r(s$^{-1}$)@Pd(111)</th>
<th>r(s$^{-1}$)@PdCu(111)</th>
<th>r(s$^{-1}$)@PdAg(111)</th>
<th>r(s$^{-1}$)@PdAu(111)</th>
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<td>0.00E+00</td>
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<td>$2.20E-04$</td>
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<tr>
<td>CCH$_3$* + H* $\leftrightarrow$ CCH$_3$H*+ *</td>
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<td>$1.42E-02$</td>
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Figure S9 Coverage of main surface species for CHCH hydrogenation as a function of temperature.
Figure S10 Relationship between activity measured by the consumption of CHCH and CHCH adsorption energy.
Figure S11 Degree of selectivity control of elementary step for CH$_2$CH$_2$ formation on Pd(111) and PdM(111) (M=Cu, Ag, Au) as a function of temperature.
Figure S12 Degree of selectivity control of elementary step for CH$_3$CH$_3$ formation on Pd(111) and PdM(111) (M=Cu, Ag, Au) as a function of temperature.

Reference

