



## Propenal Hydrogenation on Silver Surface - A Theoretical Approach

Adelaida Andoni<sup>\*,a</sup>, Rutger A. van Santen<sup>b</sup>

<sup>a</sup>Department of Chemistry, Faculty of Natural Sciences, University of Tirana, Blv. "Zog I", 1001, Tirana, Albania

<sup>b</sup>Department of Inorganic Chemistry and Catalysis, Schuit Institute of Catalysis, Eindhoven University of Technology, P.O. Box 513, 5600 MB, Eindhoven, The Netherlands

[adelaida.andoni@unitir.edu.al](mailto:adelaida.andoni@unitir.edu.al)

Catalytic reactions perform best if the interaction between the adsorbates and the surface is not too strong and not too weak. This relates to the d-band occupancy of the metals. In this respect, hydrogenation of propenal or acrolein on silver surface rises up the question whether H<sub>2</sub> proceeds in the mechanism of the reaction as molecule or dissociates on silver. Silver having an electronic configuration 4d<sup>10</sup>5s<sup>1</sup> cannot dissociate the strong bond of H<sub>2</sub>. However, it is known that even on gold provided the gold particles are very small molecules such as O<sub>2</sub> can dissociatively chemisorb. Aiming elucidation of the reaction mechanism, small clusters of silver atoms are considered (mimicking small particles) by checking first their stability by means of theoretical calculations. Next, adsorption of hydrogen was allowed in order to estimate whether the adsorption energy is exothermic or not. In this context, computational calculations carried out by means of Density Functional Theory for small silver clusters indicated that rhombic structure was the most stable configuration. Adsorption of hydrogen on rhombic silver cluster yielded negative value of the adsorption energy suggesting that hydrogen can dissociatively be adsorbed on small particle and step surfaces as well.

### 1. Introduction

Catalysts may make significant difference in reaction rate. For example, a hydrogen/oxygen mixture may be stable for years at 25 °C. Nevertheless, if one introduces a platinum wire into the mixture, the mixture explodes. Another introductory example is the key reaction in the cleaning automotive exhaust, the catalytic oxidation of CO to CO<sub>2</sub> on the surface of noble metals such as Pt, Pd, Rh and Au-Cu (Liu et al. 2011) as well as over FeOx-supported Pd catalyst (Liu et al. 2012). Reduction of CO<sub>2</sub>, on the other hand, remains challenging as recently reported (Siitonen and Ahtila, 2009). Selective catalytic hydrogenation of organic  $\alpha$ - $\beta$  unsaturated aldehydes (for example, propenal or acrolein) is a reaction with important applications in the industrial field (Bron et al. 2007). It gives the following types of products (Figure 1).

The most important product from an industrial point of view is the unsaturated alcohol, which is also the most difficult to obtain since it is known that the hydrogenation of the C=C group in  $\alpha$ - $\beta$  unsaturated aldehydes is more favourable than the hydrogenation of C=O group (Bron et al. 2007). To improve the selectivity towards the unsaturated alcohol several attempts are made to develop a catalytic system suitable for this reaction (Bron et al. 2007). It is known that monometallic silver is able to hydrogenate selectively the C=O group of  $\alpha$ - $\beta$  unsaturated aldehydes in the gas phase (silver having a low value of the heat of adsorption for hydrogen can preferentially hydrogenate the C=O group because strongly adsorbed hydrogen reacts more readily with the C=C group than weakly adsorbed hydrogen). It is assumed that the first step of the reaction is the dissociation of hydrogen on silver and the second one is the hydrogenation of double bonds C=C and C=O (Bron et al. 2007). Nevertheless from catalysis point of view, as we go from the left to the right in a row of the periodic table the tendency in the reactivity of metals changes as shown in Figure 2 (Chokendorf and Niemantsverdriet, 2003).

Please cite this article as: Andoni A., van Santen R. A., 2013, Propenal hydrogenation on silver surface-a theoretical approach, Chemical Engineering Transactions, 34, 19-24 DOI:10.3303/CET1334004

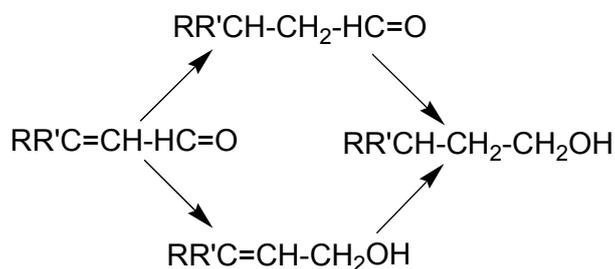


Figure 1: Schematic representation of hydrogenation of  $\alpha$ - $\beta$  unsaturated aldehydes

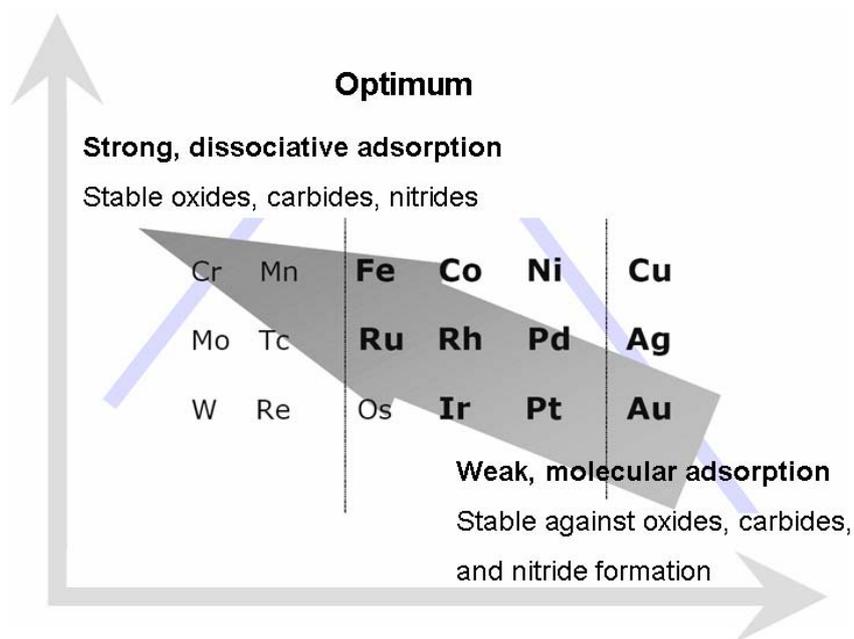
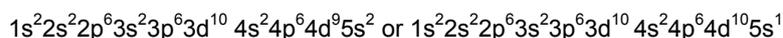


Figure 2: Part of the periodic table showing the tendency of metals to dissociate or not a chemical bond

According to the Sabatier's principle there is an optimum of the rate of the catalytic reaction as a function of the heat of the adsorption (van Santen et al. 1999). If the adsorption is too weak the catalyst will not be able to dissociate a bond. If the adsorption is too strong the adsorbates will not be able to desorb the surface. Both cases result in small rates of reactions. This relates to the d-band occupancy of the metals as follows: metals to the left of the periodic table dissociate a chemical bond but the formed atoms will be strongly bound to the surface and therefore less active. Metals to the right are unable to dissociate a chemical bond (Figure 2). This leads for an optimum for metals in the middle of the periodical table. In this context, from Figure 2 it is clear that dissociation of hydrogen on silver will not occur. The d band of silver is full ( $4d^{10}5s^1$ ). However, molecular hydrogen and oxygen are dissociatively chemisorbed on gold provided the gold particles are very small as indicated in (Chokendorf and Niemantsverdriet, 2003) and further analysed in (Hussain, 2010). Therefore, hydrogenation of acrolein on silver surfaces rises up the question whether hydrogen ( $\text{H}_2$ ) proceeds in the mechanism of the reaction as molecule or dissociates on silver catalyst and enters the reaction as atom. Aiming the elucidation of the reaction mechanism we considered small clusters of silver atoms (creating hypothetically small particles or mimicking step surfaces) by checking first their stability by means of theoretical calculations and adsorbing afterwards hydrogen in order to estimate whether the adsorption energy is exothermic or not. We modelled silver clusters based on their shape and size also. In addition to silver clusters, silver slab calculations were carried out as well.

## 2. Computation details

The energies are calculated using B3LYP Density Functional Theory (DFT). The basis set used in the calculations is LANL2DZ for 19e-ECP (effective core potential) of the GAUSSIAN98 package. The electronic configuration of silver is:



The inner part of the shell ( $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$ ) is kept frozen (LANL2) and 19 valence electrons ( $4s^2 4p^6 4d^9 5s^2$ ) are included in calculations (DZ). Additionally, VASP (Vienna ab initio Simulation Package) is also used in this work. VASP uses DFT to periodical systems and in the present work VASP was applied to slabs Ag fcc (face centred cubic). The metal-metal distance optimized with bulk calculations was 2.9 Å, which is similar with the experimental value (Andoni and van Santen, 2002). Next to bare silver surface calculations, adsorption of H on Ag was studied as well. Calculations were performed using a 2x2 supercell. The K-points sampling was generated following the Monkhorst-Pack procedure with a mesh 5x5x1. The supercells were separated in z direction by vacuum layers. 4 vacuum layers and 4 slab layers were used. The coverage of adsorbates was 0.25 monolayer (ML). The Ag and H pseudopotentials were converged with an energy cut-off for the plane-wave basis set of 350 eV.

## 3. Results and discussion

Figure 3 represents models of silver clusters of 4 to 6 atoms. The stability of silver clusters was taken into account, based on their shape, size and multiplicity also. The results of the performed calculations are shown in table 1. It is clear from Table 1 that rhombic is unambiguously the most stable geometry of  $Ag_4$ . The instability of tetrahedral configuration can be related to highly symmetrical tetrahedral  $T_d$  structure (Andoni and van Santen, 2002). The four valence electrons are insufficient to fill the degenerate one-electron levels of the highly symmetrical tetrahedral  $T_d$  structure. Such a situation necessitates a large interaction of normal mode of vibration in order for the degeneracy to be broken. Among the  $Ag_6$  clusters again the flat cluster (planar triangular) is the most stable but as our investigation focuses on dissociative adsorption of  $H_2$  on step surfaces calculations of octahedral and bipyramid structures were performed as well. The stability of the clusters depends also on multiplicity and the number of atoms (even or odd). The instability of the clusters geometries relates also, in cases of multiplicity and number of atoms, to degeneration of energy levels causing the system to change symmetry to a higher one. The next step of the calculations was the investigation of dissociative adsorption of  $H_2$  on the most stable geometries obtained based on the reaction:  $Ag_n + H_2 \rightarrow Ag - 2H$ . The results for the dissociative adsorption of  $H_2$  on Ag are tabulated in Table 2.

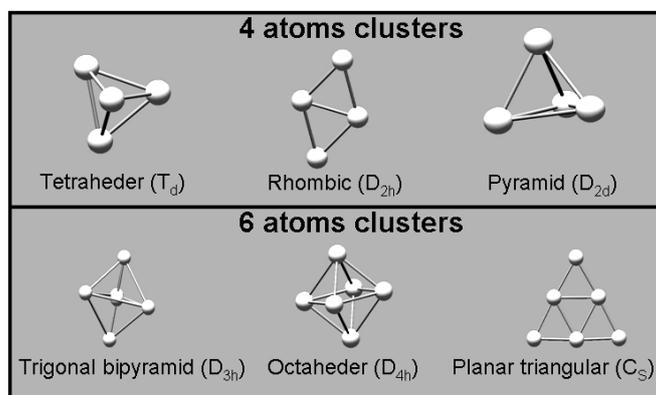


Figure 3: Models of silver clusters  $Ag_n$  ( $n=4,6$  atoms)

Table 1: Stability of silver clusters as function of size, shape and multiplicity

configuration	number of atoms	multiplicity (2S+1)	symmetry group	$E_{\text{cluster}}$ (A.U.)
rhombic	4	singlet	$D_{2H}$	-583.174
rhombic	4	triplet	$D_{2H}$	-583.150
rhombic	4	pentet	$D_{2H}$	unstable
pyramid	4	singlet	$D_{2D}$	-583.149
pyramid	4	triplet	$D_{2D}$	unstable
pyramid	4	pentet	$D_{2D}$	-583.044
tetrahedral	4	singlet	$T_D$	unstable
tetrahedral	4	triplet	$T_D$	unstable
tetrahedral	4	pentet	$T_D$	unstable
octahedral	6	singlet	$D_{4H}$	unstable
octahedral	6	triplet	$D_{4H}$	-874.761
octahedral	6	pentet	$D_{4H}$	-874.703
trigonal bipyramid	6	singlet	$D_{3H}$	unstable
trigonal bipyramid	6	triplet	$D_{3H}$	-874.714
trigonal bipyramid	6	pentet	$D_{3H}$	-874.660
planar triangular	6	singlet	$C_S$	-874.816
planar triangular	6	triplet	$C_S$	unstable
planar triangular	6	pentet	$C_S$	-874.648

Table 2: Results for dissociative adsorption of  $H_2$  on Ag clusters.

configuration	multiplicity (2S+1)	$E_{\text{ads}}$ (kcal/mol)	basis set
		$E_{\text{ads}} = E_{(\text{Ag}-2\text{H})} - (E_{\text{Ag}_n} + E_{\text{H}_2})$	
rhombic-2H	singlet	-41.26	3-21G
rhombic-2H	singlet	-5.509	LANL2DZ
planar triangular-2H	singlet	+2.7	LANL2DZ
octaheder-2H	triplet	-1.88	LANL2DZ
trigonal bipyramid-2H	triplet	-11.92	LANL2DZ

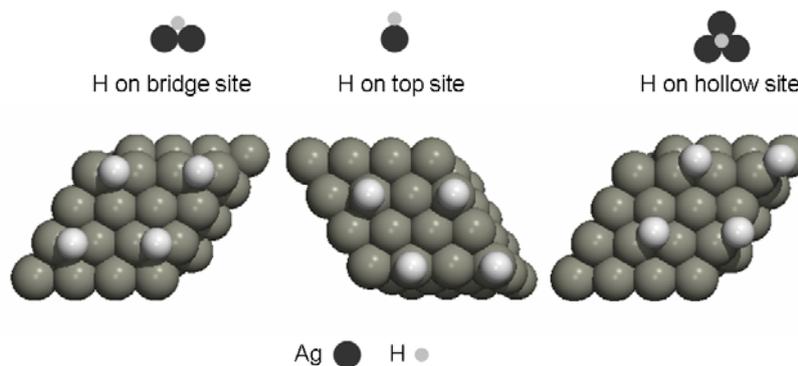


Figure 4: Slabs of silver (111) with hydrogen atoms adsorbed on bridge, top and hollow sites ( $\theta_H=0.25$  ML)

It is conclusive from Table 2 that the reaction is exothermic for rhombic, octaheder, and bipyramid clusters. The excited states for octaheder and bipyramid clusters were considered for the calculations due to the fact that triplet was the most stable state in both cases. For comparative reasons different basis set was also included in the calculation i.e. 3-21G. From our cluster model can be concluded that hydrogen can

dissociate on small particles and step surfaces. It is reported that even on gold particles provided they are small molecules such as oxygen are dissociatively chemisorbed (Chokendorf and Niemantsverdriet, 2003). This supports that assumption that in acrolein hydrogenation on silver, H<sub>2</sub> is in the first step dissociated. At any rate it is necessary to investigate the dissociative adsorption of H<sub>2</sub> on Ag slab (111) or (110) as every atom has more neighbours in slab, comparing with the cluster. We modelled in our clusters (111) surface like rhombic and planar triangular and other shapes which are similar to step surfaces. In this context we considered slab calculations for atomic hydrogen adsorbed on different sites of Ag (111) surface (Figure 4). The coverage of hydrogen is 0.25 monolayer (ML).

The obtained adsorption energies for the above slab structures are tabulated in table 3. The adsorption energy was calculated as follows:  $E_{ads} = E_{Ag-slab-H} - (E_{Ag-slab} + E_H)$  for the reaction  $Ag-slab + H \rightarrow Ag-slab-H$ . It is clear from table 3 that reactivity of H gets higher going from low to high coordination i.e. from atop to hollow sites. DFT (density functional theory) studies of H on Rh(100) indicated that hydrogen is adsorbed preferably in four-fold hollow sites (Van Bavel et al., 2012).

Table 3: Results of the adsorption energies for atomic hydrogen on slabs of Ag (111).

system	$E_{ads}$ (eV)
Ag+H atop site	-2.65
Ag+H bridge site	-3.04
Ag+H hollow site	-3.15

Lastly, adsorption energy of propenal or acrolein on silver cluster was calculated as well. The chemical structure of acrolein is drawn in Figure 5. The rhombic cluster (singlet) was considered for the calculations as the most stable structure. As the next issue of our work is the competitive adsorption between C=O and C=C, three different configurations were considered.

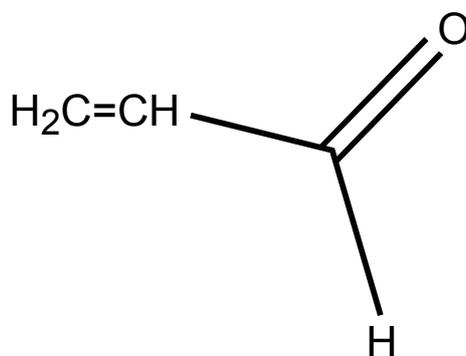


Figure 5: Schematic representation of propenal or acrolein chemical structure

The results of the different adsorption modes are summarized in table 4. The first adsorption mode entails C=O bond on Ag<sub>4</sub> whereas the second adsorption mode entails C=C bond on Ag<sub>4</sub> cluster. The adsorption energy is calculated as follows:  $E_{ads} = E_{(acrolein-Ag_4)} - (E_{Ag_4} + E_{acrolein})$  for the reaction  $Ag-slab+acrolein \rightarrow Ag-slab-acrolein$ . It is indicative from table 4 that the adsorption mode of C=O-Ag<sub>4</sub> is the preferred mode compared with the C=C-Ag<sub>4</sub> adsorption mode. This agrees well with the finding that silver exhibiting low heat of adsorption preferentially hydrogenate C=O groups (Andoni and van Santen, 2002). In addition Bron et al. (2007) reported that small Ag particles (nm range) lead to enhanced allyl alcohol formation (hydrogenation of C=O bond) whereas, the selectivity to the other main product propionaldehyde (hydrogenation of C=C bond) was reduced. This makes silver a unique catalyst for the hydrogenation of acrolein. The associative adsorption for the parallel position (including the three carbon atoms and oxygen atom as well) was also comprised in the calculations. The value  $E_{ads}=-14.18$  kcal/mol for the parallel

adsorption mode suggests this is the most preferred adsorbed configuration for acrolein on silver rhombic cluster.

*Table 4: Results of the adsorption energies for acrolein on silver cluster (rhombic structure)*

configuration	multiplicity (2S+1)	basis set	method	mode of adsorption	$E_{\text{ads}}$ (kcal/mol)
Ag <sub>4</sub> -acrolein	singlet	LANL2DZ	Becke3LYP	C=O	-5.52
Ag <sub>4</sub> -acrolein	singlet	LANL2DZ	Becke3LYP	C=C	-2.5
Ag <sub>4</sub> -acrolein	singlet	LANL2DZ	Becke3LYP	C,C,C,O	-14.18

#### 4. Conclusions

DFT calculations are carried out for small silver clusters, hydrogen adsorption on silver cluster and propenal (acrolein) adsorption on silver cluster as well. The calculations for the small silver clusters indicated rhombic structure (singlet) to be the most stable configuration. Adsorption of hydrogen on rhombic silver cluster yielded negative value of the adsorption energy suggesting that hydrogen can dissociatively be adsorbed on small particle and step surfaces as well. Although, the model is hypothetical the conclusions agree well with the reported findings in the literature (Bron et al. 2007). Additionally, it can be fairly assumed in the reaction mechanism that hydrogen can dissociatively be adsorbed on silver catalyst. Increasing the number of Ag atoms from clusters to slab, VASP calculations carried out for hydrogen adsorption on Ag slab indicated preferential adsorption on hollow sites. Lastly, DFT calculations for the adsorption of propenal on silver cluster (rhombic configuration) indicated that the adsorption mode of C=O-Ag<sub>4</sub> is the preferred mode compared with the C=C-Ag<sub>4</sub> adsorption mode.

#### References

- Liu X., Wang A., Li L., Zhang T., Mou C-Y., Lee J-F., 2011. Structural changes of Au–Cu bimetallic catalysts in CO oxidation: In situ XRD, EPR, XANES, and FT-IR, *Journal of Catalysis*, 278, 288-296.
- Liu L., Qiao B., He Y., Zhou F., Yang B., Deng Y., 2012. Catalytic co-oxidation of CO and H<sub>2</sub> over FeO<sub>x</sub>-supported Pd catalyst at low temperatures, *Journal of Catalysis*, 294, 29-36.
- Siiitonen S., Ahtila P., 2009. The influence of operational flexibility on the reduction of CO<sub>2</sub> emissions in industrial energy production, *Chemical Engineering Transactions*, 18, 63-68 DOI: 10.3303/CET0918008.
- Bron M., Teschner D., Knop-Gericke A., Jentoft F.C., Kröhnert J., Hohmeyer J., Volckmar C., Steinhauer B., Schlögl R., Claus P., 2007. Silver as acrolein hydrogenation catalyst: intricate effects of catalyst nature and reactant partial pressures, *Physical Chemistry Chemical Physics*, 9(27), 3559-3569.
- Chokendorf I., Niemantsverdriet J.W., 2003. *Concepts of Modern Catalysis and Kinetics*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany.
- Hussain A., 2010. *A Computational Study of Catalysis by Gold in Application of CO oxidation*, PhD thesis, Eindhoven University of Technology, Eindhoven, The Netherlands.
- Van Santen R.A., Van Leuwen P.W.N.M., Moulijn J.A., Averill B.A., 1999. *Catalysis: An Integrated Approach*, Elsevier, Amsterdam, The Netherlands.