Adsorption and dissociation reaction of propene on bare and yttrium doped gold clusters

Júlia Barabás,[a] **Jan Vanbuel,**[b] **Piero Ferrari,**[b] **Ewald Janssens,**[b*] **Tibor Höltzl**[a,c*]
[a]*Department of Inorganic and Analytical Chemistry, Budapest University of Technology and Economics, Budapest, H-1111, Hungary*
[b]*Laboratory of Solid State Physics and Magnetism, KU Leuven, Leuven, B-3001, Belgium*
[c]*Furukawa Electric Institute of Technology, Budapest, H-1158, Hungary*
**Corresponding author: ewald.janssens@kuleuven.be*
**Corresponding author: tibor.holtzl@furukawaelectric.com*
Presenter: julia.barabas@mail.bme.hu

Abstract: The adsorption of propene and dissociation reactions on neutral and cationic bare and yttrium doped gold clusters (n = 5-15) were studied by the combination of experiments and Density Functional Theory calculations. The results showed that the stability of the complexes and the reactivity of the clusters depends strongly on the cluster size and the presence of yttrium dopant. The analysis of chemical bonding and the orbitals implied donation/back-donation mechanism for the propene adsorption, while the analysis of EDA showed that the intermolecular interactions are the most important in the complex.

Keywords: metal clusters, tuning and design, computational chemistry

1. Introduction

In the past several decades small metal clusters have become an interesting research topic, because their physical and chemical properties are significantly different from those of the corresponding bulk material. One of the main advantages are their improved catalytic properties. Catalyst performance is generally sensitive to the particle size, hence the surface structure and electronic properties significantly change in this size range[1]. Catalytic activity of gold nanoclusters have attracted a lot of attention in recent years due to the potential applications.

Recently the gas phase reactions between neutral Au_n (n = 9-25) clusters with propene under few collision conditions demonstrated that the reaction probability for propene adsorption is larger for gold clusters composed of an even number of atoms[2]. Clusters can be a good system to catalyze the oxidation or the dissociation reaction of propylene. The improvement of a direct oxidation route of propylene towards propylene oxide would be highly desirable to decrease the energy and cost demand of this process, while dissociation reactions also result valuable chemicals. With doping we can fundamentally further modify the cluster properties, therefore numerous studies have been carried out also on doped gold clusters.

The aim of this work is to investigate the propene adsorption and dissociation on neutral and cationic bare Au_n and yttrium doped $Au_{n-1}Y$ (n = 5-15) clusters using mass spectrometry based experimental and density functional theory based computational methods.

2. Methods

The pure and the yttrium doped gold clusters are produced in a dual-target dual-laser vaporization source. The temperature of the source is controllable in the 100–300 K range by a combination of liquid nitrogen cooling and resistive heating. After expansion into vacuum and passage through a conical skimmer, a molecular beam of clusters is formed. Initially charged particles are electrostatically deflected out of the beam. The neutral clusters interact with the C_3H_6 molecules in a collision cell that is placed in the flight path of the molecular beam. In order to study the kinetics of the reaction, the pressure of the reactive gas is varied, while the interaction time is fixed by the drift time of the neutral clusters through the cell. The pressure inside the reaction cell is measured by a capacitance gauge and was varied in the range of 0–0.14 Pa, corresponding to 0–7 collisions per cluster on average. Dissociation energies were extracted using RRKM theory based on the experimentally determined dissociation rates and the computed frequencies.

Density Functional calculations were carried out using the Q-Chem 4.4 quantum chemical software package. The BP86 generalized gradient functional was applied in conjunction with the LANL2DZ basis set to pre-optimize the molecular geometries. On the optimized geometries of the most stable clusters more accurate single point calculations were carried out using hybrid TPSSh functional and the DEF2-TZVP basis set. Chemical bonding was analyzed using the Localized-Orbital Locator (LOL), Natural Charges and Wiberg bond indices. Energy decomposition and charge transfer analysis (EDA) was carried out to analyze the nature of interactions between propene and clusters and to determine the orbital interactions in the complexes. Thermochemical computations were performed using the Tamkin library.

3. Results and discussion

The experimental cluster-propene complex dissociation rates are strongly dopant and size dependent, and in general larger for the yttrium doped gold clusters, especially for larger sizes, i.e. $n > 13$. For pure gold clusters, the size dependence was already discussed in ref. [2]. The yttrium doping significantly increases the dissociation rate in the $n = 12-20$ size range. The dissociation rate coefficients show a clear odd-even alternation both for the pure and yttrium doped gold clusters, where clusters with an even number of atoms are more reactive towards propene.

DFT calculations showed that for the pure gold clusters propene binds preferentially on-top a low coordinated gold atom through its C=C double bond, which corresponds to a π-bonding mode. In the case of the $Au_{n-1}Y$ clusters, the propene binds to the yttrium atom for $n \leq 9$, while for larger clusters the propene connects to a gold atom. This adsorption site preference can be correlated with the structural evolution of the clusters with the size. It is not the case for the cationic clusters where propene binds to a gold atom for all sizes. In addition propene prefers to bind to the atom where the LUMO has the largest lobe.

The thermodynamics of the adsorption showed size dependent Gibbs free energies. We find that yttrium doping makes the complexes less stable: in this case the dissociation of propene from the cluster becomes thermodynamically favorable already in the 250-500 K temperature range, while for pure gold clusters it happens in the 500-800 K range.

The analysis of chemical bonding showed that there is no covalent bond between the cluster and the propene molecule and the adsorption has a small influence on the electronic structure. On the other hand, according to the Energy Decomposition and Charge Transfer Analysis the adsorption is dominated by intermolecular interactions. Interestingly, the yttrium induces a significant change in these interactions, as the polarization term is more important if propene binds to yttrium compared to that case where the propene connects to a gold atom.

4. Conclusions

DFT calculations confirm the experimental findings that the preference for C_3H_6 adsorption on the clusters is strongly size dependent and the yttrium doping surprisingly lowers the adsorption probability, particularly in the $x = 12-20$ size range. This study indicates donation/back-donation mechanism for the adsorption, while the reaction mechanism of propene dissociation on the clusters has also investigated. According to the Energy Decomposition and Charge Transfer Analysis the intermolecular interactions are responsible for the observed alternation of binding strength.

References

1. P. Serp, K. Philippot; Nanomaterials in Catalysis, Wiley-VCH Verlag GmbH & Co. KgaA, 2013.
2. E. Janssens, H. T. Le, P. Lievens, Chem. Eur. J 21 (2015) 15256.