

Adsorption of CO molecules on MAu_nO₂⁺ oxidized doped gold clusters (M = Ti, Fe; n = 1, 4-7). A theoretical DFT study

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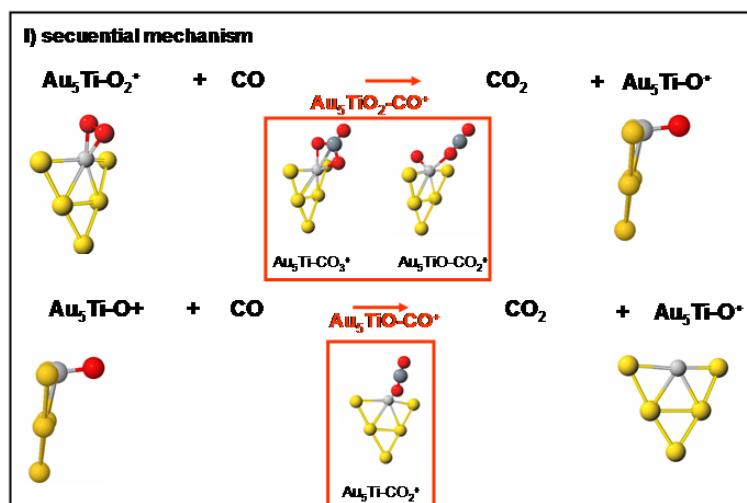
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Abstract – We have studied the adsorption of CO molecules on several low lying energy isomers of MAu_nO₂⁺ clusters (M=Ti, Fe; n= 1, 4-7). These isomers were previously obtained in a study of the adsorption of O₂ on MAu_n⁺ clusters¹. The present work is based on first-principles calculations using the Siesta code² within the spin dependent PBE-GGA³. Norm conserving pseudopotentials and multiple-zeta basis sets for this problem were tested and used as in previous works¹. Auxiliary tools to find the transition state and reaction barriers have been taken from the Gaussian code⁴ and from the ASE interface⁵ to the Nudged Elastic Band (NBE) method.

Two different CO adsorption mechanisms are considered: i) sequential, and ii) simultaneous. In the case i), the adsorption of a CO on Au_nMO₂⁺ leads to the formation of Au_nMO⁺ cluster and a CO₂ desorbed molecule. Then, a second CO molecule is adsorbed on the product Au_nMO⁺, and a second CO₂ is desorbed, leading to the clean MAu_n⁺ cluster. This mechanism involves the calculation of several reaction intermediates for each one of the steps, as shown in the Figure 1 for M=Ti and n=5. In a number of cases we have calculated the vibration frequencies of these complexes to distinguish between reaction intermediates and transition states. Intrinsic reaction coordinate (IRC) calculations are also performed so that a transition state connects two appropriate local minima in the reaction pathway.

Figure 1: Scheme for the two steps sequential adsorption of CO molecules on oxidized Au₅Ti-O_x⁺ gold clusters doped with a Ti atom. In the first step (x=2) a CO₂ molecule is desorbed leaving an Au₅Ti-O⁺ cluster. In the second step another CO molecule is adsorbed on the product Au₅Ti-O⁺ and a second CO₂ molecule is desorbed leaving the clean Au₅Ti⁺ cluster. Several intermediate complexes are produced. Energy barriers and transition states are analyzed using state of the art methods.



In the mechanism ii) we have optimized complexes of the type [MAu_nO₂⁻ (CO)₂⁺] from which two CO₂ can be desorbed leading to the clean MAu_n⁺. Among these complexes can be highlighted a) MAu_n-C₂O₄⁺, with the oxalate C₂O₄ bonded to M, and b) MAu_n-(CO₂)₂⁺, with two preformed CO₂ molecules bonded to M. The calculations of IRC pathway and vibration frequencies for selected complexes are in progress.

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References

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