

Study of atomic clusters revealed new mechanisms for low-temperature transformations of very stable molecules

Funded by the National Natural Science Foundation of China and Chinese Academy of Sciences (CAS), Dr. He Shenggui and his colleagues from Institute of Chemistry, CAS, investigated the mechanisms for low-temperature (LT) transformations of very stable molecules with a bottom-up strategy; they systematically generated atomic clusters composed of different numbers of atoms and different kinds of elements and observed the cluster reactivity toward small molecules at room temperature (RT) by home-made mass spectrometers under isolated, controlled, and well reproducible conditions. The observed cluster reactivity has been well interpreted on the basis of quantum chemistry computations and simulations with molecular reaction dynamics. The interplay between theory and experiment is intriguing because the two methods were used to handle exactly the same system with known elements and known number of atoms.

By introducing gold atoms into the O^- containing clusters, He's group observed the rarely reported activation of multiple C-H bonds with high selectivity; double hydrogen atom abstraction (HAA) from ethane and triple HAA from *n*-butane by the AuNbO_3^+ cluster ions (*Angew Chem Int Ed*, **2013**, 52; 2444–2448). The multiple HAA is initiated by the O^- radicals and promoted by gold. Gold atom acts as electron acceptor during the triple HAA and helps to store a pair of valence electrons in between Au and Nb atoms (Figure 1). Such pair of electrons can be released to reduce molecular oxygen. The cluster study revealed the nature of gold activity. The promotion of gold in the multiple HAA reactions can be traced back to the relativistic effect in Physics.

The researchers in He's laboratory generated the O^- bonded titanium and zirconium nano-particles $(\text{MO}_2)_n\text{O}$ ($\text{M} = \text{Ti}, \text{Zr}$) in the gas phase and characterized their reactivity with CO at RT. The oxygen atom transfers from titanium oxides to CO (formation of gaseous CO_2) were observed, whereas the reactions of zirconium counterparts with CO generated the CO addition products (formation of adsorbed CO_2), which lost CO_2 upon the collisions with a crossed helium beam (*J Am Chem Soc*, **2013**, 135; 2991–2998). The cluster study addressed different behaviors of the supports in Au/MO_2 ($\text{M} = \text{Ti}, \text{Zr}$) catalysts and provided evidence for involvement of the O^- radicals in LT CO oxidation. The different reactivity of Ti versus Zr systems can be traced back to lower Ti 3d versus Zr 4d orbitals (Figure 2).

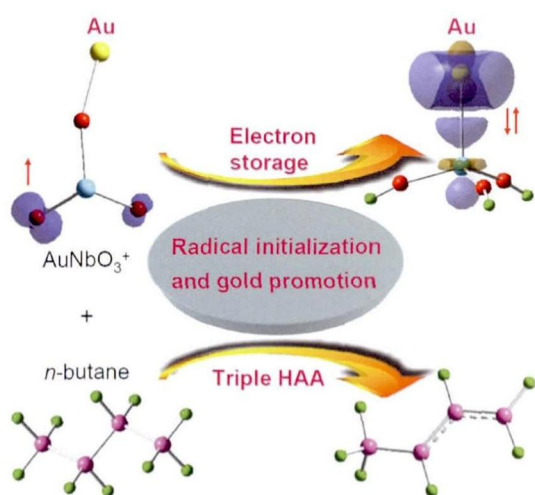


Figure 1 Storage of valence electrons by gold during the triple HAA.

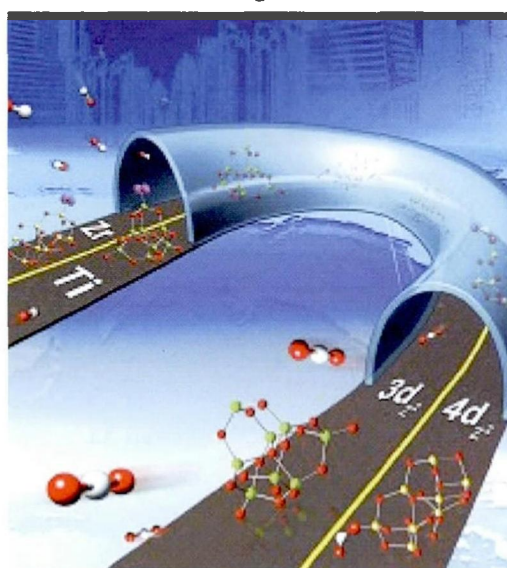


Figure 2 Valence d orbitals make difference in CO oxidation