

## Chemical Reactivity and Nano catalysis

---

Dr.M.Manoranjani<sup>1</sup>,Dr.C.A.Jyothirmayee<sup>2</sup>,Kola.Sushma<sup>1</sup>,Paleru.Par  
dhu<sup>1</sup>,Musunuru.Hima Priya<sup>1</sup>, Reddy.Manideep<sup>1</sup>

1.PG Dept. of Chemistry P.B.Siddhartha College of Arts & Science,  
Vijayawada.

2.Ch.S.D.St.Theresa's autonomous College for women, Eluru.

---

### **Abstract:**

Gold is one of the most interesting and mysterious materials with unique catalytic properties emerging at nanoscale. The large interest to gold Nano catalysis is stipulated by the fact that nanoparticles of gold demonstrate extraordinary catalytic activity and selectivity even at room temperatures. The reactions of oxidation catalysed by the small gold nanoparticles are of particular interest, because the molecular oxygen from the air can play a role of the oxidant, making the whole process to be an ideal and waist free reaction. Development of effective and environment friendly catalysts based on abundant elements for energy and environment related applications is emerging task. Instead of investigation of the well-known and well-studied catalytic materials based on the precious metals, like Pt, Pd, Ru, etc. we are keen to study how to functionalize abundant catalytically inactive or even completely inert nanomaterials and control their catalytic properties (activity, selectivity) via support design and morphology.

**Keywords:** Mysterious, Morphology, ideal and waist free reaction.

### **Gold nano catalysis**

Gold is one of the most interesting and mysterious materials with unique catalytic properties emerging at nanoscale. The large interest

---

to gold Nano catalysis is stipulated by the fact that nanoparticles of gold demonstrate extraordinary catalytic activity and selectivity even at room temperatures. The reactions of oxidation catalysed by the small gold nanoparticles are of particular interest, because the molecular oxygen from the air can play a role of the oxidant, making the whole process to be an ideal and waist free reaction. This feature is important for many industrial and green chemistry applications. There are several factors that can affect catalytic properties of nanoparticles. Among them the size, the geometry structure and morphology, the charge state of nanoparticle, the support effects, etc. To create new catalytic materials by design at the nano-level it is necessary to predict how these factors affect the catalytic properties of nanoparticles.

#### **Reactivity of free clusters**

Catalytic activation of the adsorbed O<sub>2</sub> on small pure gold clusters cannot lead to its dissociation. However, Coad sorption of simple hydrocarbons, such as ethylene, C<sub>2</sub>H<sub>4</sub>, results in extra charge transfer from the gold cluster to O<sub>2</sub>, energetically promoting oxygen dissociation. Therefore, O<sub>2</sub> dissociation on the surface of small gold clusters is sensitive to the presence of other adsorbents, including the reactant molecule itself. This effect can be particularly important for understanding the mechanism of catalytic oxidation on gold clusters. We have also found an effect of the cooperative adsorption of O<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> on small gold clusters. This finding indicates that the process of oxygen dissociation on the surface of gold clusters is sensitive to the presence of other adsorbates, including the reactant molecule itself.

Adsorption of ethylene molecules on neutral, anionic, and cationic gold clusters demonstrates very interesting features. Thus, C<sub>2</sub>H<sub>4</sub> can be adsorbed on small gold clusters in two different configurations, corresponding to the  $\pi$ - and di- $\sigma$ -bonded species. Adsorption in the  $\pi$ -bonded mode dominates over the di- $\sigma$  mode over all considered cluster sizes  $n \leq 10$ , with the exception of the neutral C<sub>2</sub>H<sub>4</sub>-Au<sub>5</sub>

system. A striking difference is found in the size dependence of the adsorption energy of  $C_2H_4$  bonded to the neutral gold clusters in the  $\pi$  and di- $\sigma$  configurations. The electronic shell effects play an important role for the di- $\sigma$  mode of ethylene adsorption on neutral gold clusters. The interaction of  $C_2H_4$  with small gold clusters strongly depends on their charge. The typical shift in the vibrational frequencies of  $C_2H_4$  adsorbed in the  $\pi$  and the di- $\sigma$  configurations gives a guidance to experimentally distinguish between the two modes of adsorption.

### **Reactivity of supported clusters**

Support effect is one of the most important factors in nanocatalysis. Therefore, a large part of our work is devoted to the theoretical analysis of the catalytic activity of the supported clusters. Hexagonal boron nitride (H-BN) surface which was traditionally considered as an inert support can strongly modify properties of the gold clusters and act as an “active” support. In particular, the structural, electronic, and catalytic properties of Au and  $Au_2$  supported on the pristine and defected H-BN surface have been studied. It is demonstrated that adsorption and catalytic activation of  $O_2$  on the H-BN supported Au and  $Au_2$  can be affected by the interaction with the support via electron pushing and donor/acceptor mechanisms. It is shown that even weak interaction of Au and  $Au_2$  with the defect-free “inert” H-BN surface can have an unusually strong influence on the binding and catalytic activation of the molecular oxygen. This effect occurs due to the mixing of the 5d orbitals of the supported Au and  $Au_2$  with the N- $p_z$  orbitals. Although the defect-free h-BN surface does not act as a good electron donor for the supported  $O_2$ -Au, it promotes an electron transfer from the  $Au$  to  $O_2$ , pushing electrons from the gold to the adsorbed oxygen. In the case of the defected H-BN surface, Au and  $Au_2$  can be trapped effectively by N or B vacancy and impurity point defects. Strong adsorption on the surface defects is accompanied by the large charge transfer to/from the adsorbate. The excess of the positive or negative charge on the supported Au and

Au<sub>2</sub> can considerably promote their catalytic activity. Therefore, the h-BN surface (pristine or defected) cannot be considered as an inert support for Au and Au<sub>2</sub>.

**Theoretical design of effective catalysts based on abundant elements for sustainable energy generation. Pt-free catalysts for fuel cell technology.**

Development of effective and environment friendly catalysts based on abundant elements for energy and environment related applications is emerging task. Instead of investigation of the well-known and well-studied catalytic materials based on the precious metals, like Pt, Pd, Ru, etc. we are keen to study how to functionalize abundant catalytically inactive or even completely inert nanomaterials and control their catalytic properties (activity, selectivity) via support design and morphology. The exciting example demonstrating credibility of the proposed approach is our recent progress on theoretical prediction of functionalization of the hexagonal boron nitride (H-BN) based nanomaterials for the oxygen reduction reaction (ORR). The ORR is a key process that allows fuel cells to operate. Currently the most efficient catalysts for ORR are based on precious metals, such as platinum. The relatively low efficiency of the known ORR catalysts, voltage losses at the cathode, the high cost and limited resources of platinum prevent the wide use of fuel cells in practical applications. We have demonstrated absolutely novel and fascinating effect: an inert H-BN monolayer can be functionalized by the nitrogen doping or by the metal support and become catalytically active for ORR. The energetics of adsorption of ORR intermediates, such as, O<sub>2</sub>, O, OH, OOH, and H<sub>2</sub>O on N-doped H-BN monolayer is quite similar to that known for a Pt(III) surface. Analysis of the free energy changes along the ORR pathway allows us to suggest that a N-doped H-BN monolayer can demonstrate catalytic properties for the ORR under the condition that electron transport to the catalytically active centre is provided. The Ni(III) support can critically change the chemical and physical properties of

defect-free monolayer h-BN, considerably promoting the adsorption of ORR intermediates, and therefore, H-BN/Ni(III) system can be catalytically active for the ORR. The described effect occurs due to the mixing of the  $d_{z^2}$  orbitals of the transition metal support with the  $N-p_z$  and  $B-p_z$  orbitals of H-BN. Although simple potential-dependent modelling of the energetics of the ORR on H-BN/Ni(III) indicates the limitation of the ORR process due to the large over potential, our calculations demonstrate principal ability to functionalize inert materials for the ORR and open new ways to design effective precious metal free catalysts based on materials never been considered as catalysts before.

When boron nitride (BN), which is originally an insulating material, is placed on a gold surface, it can function as an electrocatalyst for ORR. We have discovered that when BN is placed on a gold surface, its electronic state changes in such a way that BN can function as an oxygen-reduction catalyst. In the group of Prof. Uosaki various types of BN (e.g. nanosheets, nanotubes) were placed on a gold surface, and examined towards their activity for the oxygen-reduction reaction by a rotating disk electrode. They observed a maximum of about 270 mV positive shift for oxygen reduction current to be observed at the gold electrode. On the other hand, no such catalyst activity was observed when a carbon was used as the substrate. Thus, we have demonstrated that BN-gold interaction is a key factor for BN to function as an electro catalyst for the ORR. Although the new catalyst is still less reactive than platinum, we succeeded in showing an extremely promising direction in the process of searching for and designing a new catalyst material, through the combination of theoretical calculation and experiments. This approach is expected to lead to the future development of materials for an electrode for fuel cells without using platinum.

