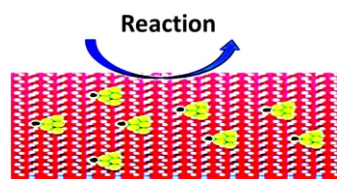


## Design and Development

8

## Single Atom Alloy Catalysis: Perception and Design

Sandeep Nigam<sup>\*1,2</sup> and Chiranjib Majumder<sup>1,2</sup><sup>1</sup>Chemistry Division, Bhabha Atomic Research Centre (BARC), Trombay-400085, INDIA<sup>2</sup>Homi Bhabha National Institute, Anushaktinagar, Mumbai-400094, INDIA

Atoms are dispersed on support

## ABSTRACT

Catalytic materials are crucial for energy and environmental sustainability. Computational material science has been indispensable tool to design novel and efficient catalytic material. Single atom catalysis is based on the philosophy maximizing the efficiency of catalyst. The present article provides a general introduction to newly emerging area 'Single-Atom Alloy Catalysts (SAAC)'. Afterwards our computational attempt in designing single atom alloy catalyst for sulfuric acid decomposition reaction (*most endothermic step of Sulfur-Iodine (S-I) thermochemical cycle*), is presented.

KEYWORDS: Single Atom Alloy catalyst, DFT, SI cycle, Ag-Pt cluster, Pt(111) slab

## Introduction

Catalysis is a kinetic phenomenon where catalytic material alters the rate of a chemical reaction, ideally without being chemically changing itself. Catalysis and Catalytic material designing are strategic field for development of newer technologies benefiting the society and this field play key role in reducing energy consumption/cost in industry. Well-known examples of catalysis are Haber process for the ammonia synthesis, contact process for sulfuric acid production, utilization of catalysts for petroleum cracking. Other than energy applications, catalytic materials are also equally important for environmental applications such as abatement of pollutants, volatile organic compounds (VOC). Industry uses various catalytic converters and smokestack scrubbers to help keep sulphur pollutants out of the atmosphere. Transport vehicle uses automotive catalytic converters to reduce the content of toxic gases and pollutants in their exhaust gas.

According to the phases in which a catalyst and the reactant(s) are present, catalysis can be classified as homogeneous, heterogeneous or biological/enzymatic. The areas of catalysis, surface chemistry have been of interest in the departmental activities of DAE i.e. catalysts for hydrogen mitigation under LOCA condition in nuclear reactor, or catalyst for D/H isotope exchange under bi-thermal condition. Schematic presented in Fig.1 summarizes the various catalysis processes being pursued in Department of Atomic Energy (DAE). In past, both homogenous Catalysis (Suzuki C-C cross coupling case) and heterogeneous catalysis (nanoparticles on oxide support) has been pursued in the DAE and presently also, department has various programs to design and development of novel catalytic materials with improved efficiencies for various energy and environmental application.

Homogeneous catalysts usually possess superior activity and/or selectivity but the major issue of separating catalyst from raw materials and products limits their real application.

Molecular-level understanding of heterogeneous catalysis tells that when a solid catalyst is used to speed up a chemical process, the overall reaction usually consists of a series of elementary steps such as adsorption of the reactants on the surface of the solid, diffusion on the surface, breaking of some reactant bonds, and the creation of new ones to form the product molecules, which eventually desorb from the surface. Due to this heterogeneous catalyst always exhibit lower atom efficiency in the catalytic process. To combine the advantages of both heterogeneous and homogeneous catalysts, Single-atom catalysts (SAC) emerging as a new area in the catalysis community [1-4].

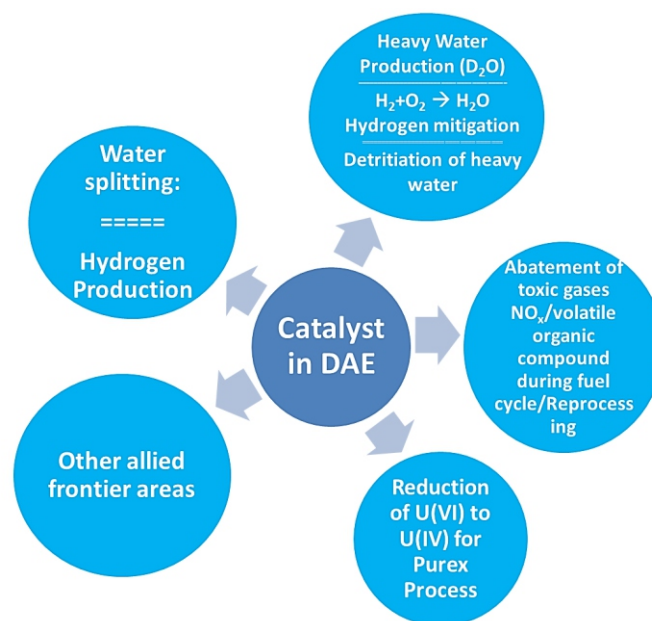


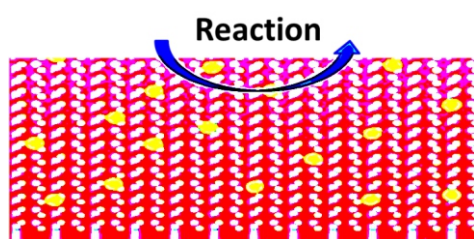
Fig.1: Schematic diagram showing some of the catalytic processes being pursued in DAE.

\*Author for Correspondence: Sandeep Nigam  
E-mail: snigam@barc.gov.in

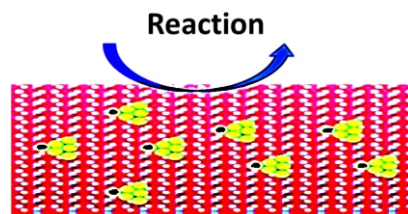
Single atom catalyst (SAC) is a catalyst where isolated atoms are dispersed over a support [1-3]. During the last decade this field of research has attracted a great deal of attention because of two reasons (1) High catalytic activity (2) Selectivity. More importantly, the dramatic development in this research activity can be explained by two reasons; (a) It can bridge the homogenous and heterogeneous catalysis (b) Linking the theoretical results with experimental observation more efficiently. While the higher selectivity can be linked to the geometrical feature like reducing ensemble effect, the higher catalytic activity is linked to the electronic structure of the narrow (localized) band d-orbital electrons of metal. Therefore, single atom catalysts are emergent catalytic materials that have the promise of merging the scalability of heterogeneous catalysis with higher activity of homogenous catalysts.

Broadly the SAC-field can be divided into three classes:

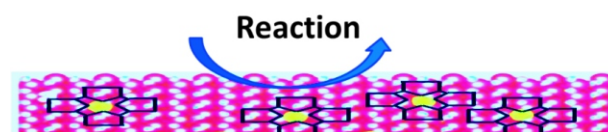
- (1) Atoms are dispersed on support (metal oxide, carbon materials etc.)



- (2) Active metal atoms are embedded into another less reactive host metal matrix i.e., Single Atom Alloy (SAA) catalyst. The alloy may be utilized as such or on some support. The following schematic shows black circle as active atom alloy with reactive host metal matrix presented in yellow.



- (3) Organometallic compounds with active metal atoms connected to ligands are deposited on support like metal oxide, carbon, MoS<sub>2</sub> etc.



In the coming sections we will be summarizing our previous effort in designing the single atom alloy catalyst for SO<sub>3</sub> decomposition reaction, the most endothermic step of Sulfur-Iodine (S-I) thermochemical cycle [4].

## Computational Method

Calculations under Density Functional Theory (DFT) formalism were performed using Vienna ab initio Simulation Package (VASP) software. Plane wave based pseudo-potential approach has been utilized for calculations. The full-potential all-electron projector augmented wave (PAW) method were used to define electron-ion interactions. The PAW pseudo-potential was generated taking scalar relativistic corrections

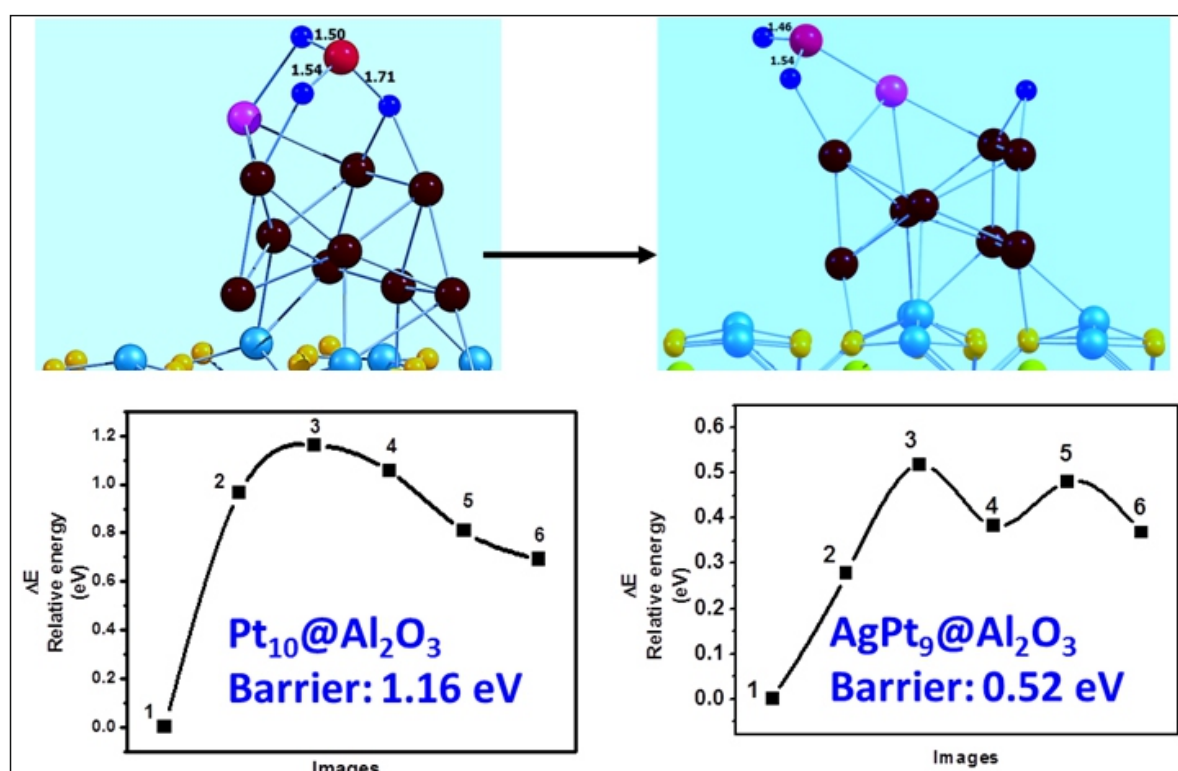


Fig.2: Reaction barrier for SO<sub>3</sub> decomposition for Pt<sub>10</sub>@Al<sub>2</sub>O<sub>3</sub> and AgPt<sub>9</sub>@Al<sub>2</sub>O<sub>3</sub> clusters.

into account. Spin polarized generalized gradient approximation has been employed to calculate the exchange-correlation energy. After spin polarized calculations, all the obtained structures were re-optimized by including spin orbit coupling (SOC). The plane wave basis set cut off energy was fixed at 400 eV. The total energy convergence was tested with respect to simulation cell size and plane-wave basis set size. The geometry optimization has been carried out by using conjugate gradient method. The geometries are considered to be converged when the forces on each ion becomes 0.01eV/Å or less. The total energy was found to be accurate within 1 meV.

### Results and Discussion

The Sulfur-Iodine (S-I) thermochemical cycle is being pursued in the DAE for large scale hydrogen generation. Chemistry Division, BARC has been working on design and development of catalyst for sulfuric acid decomposition reaction, the most endothermic step of Sulfur-Iodine (S-I) thermochemical cycle [5]. Comparative studies on iron oxide-based catalysts ( $\text{Fe}_2\text{O}_3$  &  $\text{Fe}_{1.8}\text{Cr}_{0.2}\text{O}_3$ ) and Pt catalyst ( $\text{Pt}/\text{Al}_2\text{O}_3$ ) have been demonstrated previously [5]. Even though, commercial Pt-based catalysts are considered to be the most promising candidates, thermal sintering and loss of Pt in the corrosive reaction environment limits their application and hunt for alternative are on. Another possible way to avoid sintering can be doping in the platinum catalyst itself. It is well known that the incorporation of an impurity atom can lead to reordering of the energy levels and thereby altering the geometry and chemical properties of catalyst. Thus, by appropriate doping the platinum catalyst, one can have the possibility of reducing the activation barrier, and simultaneously one can play with nanocluster support interaction as well. Reduction of activation barrier can help in reducing the reaction temperature, while improved platinum support interaction can enhance the binding and its sustainability during the reaction condition. In this context, single atom alloy catalyst can play a big role in optimizing the performance of Pt catalyst for  $\text{SO}_3$  decomposition. Specific question attempted were

- (1). Can one bring down the  $\text{SO}_3$  decomposition reaction temperature by reducing the activation barrier?
- (2). Can one increase the sintering resistance?

With this motif, we theoretically investigated the potential of single Ag site embedded Pt catalyst towards  $\text{SO}_3$  decomposition [4]. Two types of substrate were considered (i) Pt nanocluster supported on alumina i.e.  $\text{Pt}_{10}/\text{Al}_2\text{O}_3$  (ii) Pt(111) surface. The selection of substrates was guided by the fact that Pt nanoparticle (~2-3 nm) on alumina support have been successfully employed as catalysts for sulfuric acid decomposition reaction and (111) facet of Pt surface is thermodynamically most stable facet therefore any platinum nanoparticle is expected to have majority of its surface as (111) facet. In order to create single atom alloy (*very low molar fraction*) catalyst from supported  $\text{Pt}_{10}$  cluster, substitutional doping of single Ag atom into  $\text{Pt}_{10}$  was carried out.

Implanting single Ag atom in alumina supported platinum cluster  $\text{Pt}_{10}/\text{Al}_2\text{O}_3$  i.e.  $\text{AgPt}_9/\text{Al}_2\text{O}_3$  leads to significantly reduced activation barrier for S-O bond breaking [4]. After interaction, S-O bond length of  $\text{SO}_3$  molecule connected to trigonal face of metal cluster ( $\text{AgPt}_9/\text{Al}_2\text{O}_3$ ) increases from 1.44 to 1.71 Å (~19% elongation). Reaction enthalpy for the decomposition reaction ( $\text{DH}_{\text{diss}}-\text{AgPt}$ ) was found to be +0.37 eV which was much lower than that of  $\text{Pt}_{10}/\text{Al}_2\text{O}_3$  counterpart ( $\text{DH}_{\text{diss}}-\text{Pt} = +0.69$  eV). Moreover, the S-O bond breaking reaction barrier (activation barrier) for  $\text{SO}_3-(\text{AgPt}_9/\text{Al}_2\text{O}_3)$  obtained under similar methodology was

0.52 eV only, i.e.; almost half of barrier obtained for  $\text{SO}_3-(\text{Pt}_{10}/\text{Al}_2\text{O}_3)$  complex. Alloying the alumina supported platinum nanocluster with single Ag atom, lowered the activation barrier for S-O bond breaking by more than 50% in comparison to pristine platinum counterpart. At variance with pure  $\text{Pt}_{10}/\text{Al}_2\text{O}_3$  which tries to detach with support during decomposition reaction, single atom alloy nanocluster  $\text{AgPt}_9/\text{Al}_2\text{O}_3$  enhances binding with support, strengthening sintering resistance. Ag weakens the binding of reaction product  $\text{SO}_2$  with cluster which can help in easy desorption (Better recyclability). During the interaction of  $\text{SO}_3$  with  $\text{AgPt}_9/\text{Al}_2\text{O}_3$ , decrease in the metal cluster-alumina surface separation was observed i.e., stronger grip of cluster on substrate. Hence, one can infer that  $\text{AgPt}_9$  cluster remains immobilized on  $\text{Al}_2\text{O}_3$  support during the reaction and expected to be resilient towards possible sintering.

After establishing the fact that presence of single Ag atom in the Pt nano cluster significantly improves its potential as catalyst for  $\text{SO}_3$  decomposition, in order to further ascertain the role of single Ag site, interaction of  $\text{SO}_3$  was investigated with Pt(111) surface before and after single atom alloying (substitutional doping with Ag). For single atom alloy catalyst, one of platinum atom in the uppermost layer was replaced with silver atom leading to 1% silver concentration in total slab. Results reveal that activation barrier for  $\text{SO}_3$  decomposition on  $\text{Ag}_1\text{Pt}(111)$  surface was 1.22 eV reduced by ~30% to facilitate the S-O bond breaking and simultaneously presence of Ag leads to weaker binding of reaction product. Notable influence of single Ag atom was also observed at both length scale i.e.  $\text{AgPt}_9/\text{Al}_2\text{O}_3$  cluster and Pt(111) slab, where it was found that single Ag atom substitution shows significant reduction in activation barrier in contrast to pristine counterpart. Single Ag atom plays dual role as it not only reduced the activation barrier but simultaneously adsorbs reaction product  $\text{SO}_2$  weakly, signifying relatively easier desorption and better recyclability. In order to rationalize the role of silver attention was focused on bonding in  $\text{SO}_3$  molecule with catalyst and deeper location of silver *d*-electrons and lesser electronegativity of silver were attributed for better performance of single Ag atom alloy Pt catalyst. When  $\text{SO}_3/\text{SO}_2$  molecule interacts with silver atoms, higher binding energy of *d*-electron of silver prevents its effective interaction with LUMO of incoming molecule which in turn weakens bonding. At the same time, the higher electronegativity difference between Ag and S leads to injection of more (relative to Pt-case) charge into sulphur atom of  $\text{SO}_3$  [4]. The more injection of charge populates an antibonding molecular orbital of  $\text{SO}_3$ , leading to elongation of the S-O bond and hence weakening of bond i.e., reduction of bond cleavage barrier.

### Conclusions

In summary, the present article has provided a brief introductory overview of Single Atom Alloy Catalyst (SAAC) and further, design of SAAC catalyst for SI-thermochemical cycle using state of the art density functional theory (DFT) has been presented. Alloying the platinum catalytic particle with single Ag atom significantly reduced the activation barrier for  $\text{SO}_3$  decomposition with better prospects of recyclability and sintering resistance. In the context of disintegrative leaching and sintering issues of the supported platinum nanoparticle catalyst, it is predicted that alloying the Pt-catalyst with low concentration Ag implanting can be very fruitful.

### Acknowledgements

The authors gratefully acknowledge the guidance and constant support provided by Dr. A. K. Tyagi Director, Chemistry Group. We are thankful to the members of the Computer

Division, BARC, for their kind cooperation during our computational investigations.

### References

- [1] Ryan T. Hannagan, Georgios Giannakakis, Maria Flytzani-Stephanopoulos, and E. Charles H. Sykes, Single-Atom Alloy Catalysis, *Chem. Rev.* 120, (2020) 12044–12088.
- [2] Selina K. Kaiser, Zupeng Chen, Dario Faust Akl, Sharon Mitchell, and Javier Pérez-Ramírez, Single-Atom Catalysts across the Periodic Table, *Chem. Rev.* 120, (2020) 11703–11809.
- [3] Lichen Liu and Avelino Corma, Metal Catalysts for Heterogeneous Catalysis: From Single Atoms to Nanoclusters and Nanoparticles, *Chem. Rev.* 118, (2018) 4981–5079.
- [4] Sandeep Nigam and Chiranjib Majumder, Single atom alloy catalyst for SO<sub>3</sub> decomposition: enhancement of platinum catalyst's performance by Ag atom embedding. *Nanoscale*, 10, (2018) 20599–20610.
- [5] A.M. Banerjee, M.R. Pai, A.K. Tripathi, S.R. Bharadwaj, D. Das and P.K. Sinha Development of Catalyst for Decomposition of Sulfuric Acid: The Energy Intensive Step in Sulfur-Iodine Thermochemical Cycle for Hydrogen Generation using Nuclear Heat, *BARC Newsletter*, 332 (2013)7-12.