Project Title:

DFT Investigation of novel materials for green energy applications

Names:

○Mohammad Hussein Naseef AL ASSADI (1), Kabir Salihu SURAJ (1)

Laboratory at RIKEN:

(1) Spin Physics Theory Research Team, Center for Emergent Matter Science

1. Background and purpose of the project:

We investigated the possible detrimental effect of metal/support orbital hybridization on the catalytic activities of heterogeneous catalysts and offered remedies. Such hybridization becomes more significant as the active catalytic particles become smaller and, therefore, require careful control. As current conventional practice recommends ever finer nano-catalysts to increase surface area for higher yields, the proposed investigations become indispensable for realizing new materials for generating commercially viable green hydrogen by balancing competing physical phenomena.

2. Specific usage status of the system and calculation method

Simulations studied here were carried out using density functional theory with GGA+U formalism and based on the Augmented plane-wave (PAW) method. The suitability and accuracy of the GGA+U method for oxides and heterostructures have been widely established. The high throughput calculations across all structures and composition spaces were automated using the *qmpy* python code. Transport properties were calculated using the *Boltztrap* code that utilizes the Boltzmann transport equation.

3. Result

So far, three nano-catalysts have been investigated: palladium, nickel, and europium nanosheets in a few layer thicknesses deposited on various substrates (Fig. 1). In summary, the study involved using density functional theory to analyze the density of states and electronic properties of palladium, nickel, and europium nanosheets containing 1, 2, and 4 atomic sheets. These nanosheets have different layer thicknesses and are deposited on various substrates, such as titania and silica, providing a comprehensive exploration of their catalytic potential. The use of DFT allows the understanding of how these nano-catalysts behave at the atomic and electronic levels, aiding in the design and optimization of catalytic materials for green energy applications.

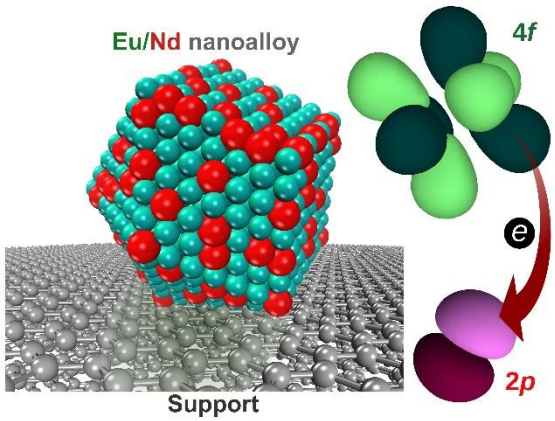

Fig. 1. Schematics of Metal nano-catalyst on a substrate.

4. Conclusion

In summary, our research findings highlight several critical insights related to different nano-catalysts:

Europium Nanosheets on Rutile Titania:

- Surface 4*f* states on Europium nanosheets, deposited on rutile titania, become sharper and move deeper into the valence band as they are located farther from the interfacial oxygen.
- This trend is more pronounced in thicker nanosheets.
- The distribution of density of states (DOS) is found to be detrimental to catalytic hydrogen production reactions that require redox behavior, such as water

splitting and hydrocarbon reforming.

- Redox reactions are more effectively facilitated by 4*f* electrons closer to the Fermi level.
- As a result, the study suggests that Europium catalysts should be synthesized as thin as possible to optimize catalytic performance.

Nickel Nanosheets on Strontium Oxide (Ni/SrO_2 Nanostructures):

- This study emphasized the critical role of the size of Nickel nanosheets in enhancing the catalytic performance of Ni/SrO_2 nanostructures for hydrogen production.
- Ni-O 3*d*-2*p* hybridization sets an optimum amount of two Ni layers that can be interfaced with SrO_2.
- Immaculate control over the synthesis of Ni nanoparticle size is crucial for improved catalysis.

Single Atom Palladium (Pd_{SA}) on Mesoporous Silica:

- Electronic interaction between single-atom Palladium and different functional groups on mesoporous silica was investigated.
- The position of Pd's 4*d* states with respect to the Fermi level explains the catalytic behavior.
- Closer concentration of Pd's 4*d* states to the Fermi level enhances catalytic activity.
- Pd-ligand bonding influences catalytic behavior: (A) Little to no charge transfer or Pd ion aggregation (metallic nanoparticles) promotes catalysis (as observed with amine functional groups); (B) More ionic bonding pulls Pd's 4d states to deeper energy levels, hindering catalysis (as observed with thiol groups).
- Stronger Pd-ligand bonding also prevents Pd aggregation into metallic nanoparticles.

In conclusion, the research underscores the significance of nano-catalyst properties, such as thickness, size, and electronic interactions, in influencing catalytic performance for specific reactions, providing valuable insights for the design and optimization of catalyst materials.

5. Schedule and prospect for the future

This investigation will be ongoing throughout the following year. The simulations proposed and conducted here are an integral part of a grant proposal funded by JST's EIG CONCERT-Japan framework entitled "Machine-learning-driven bottom-up design of atomically layered heterostructures for green H_2 production (MLALH)". *The simulations conducted on the Hokusai machine have produced two submitted manuscripts and two submitted conference proceedings to be published soon*.

6. If no job was executed, specify the reason.

Not Applicable.