**On the Strong Metal Support Interaction (SMSI( state**

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**Abstract**

Any catalyst scientist aims to design a effective and selective catalyst for the chosen reaction**.** Strong Metal Support Interaction state is one of the attempts in literature to fulfill this utopian dream. These systems by simple physical treatment alters the activity for hydrogen and carbon monoxide reactions and also can be used in energy conversion devices.

**1.Introduction**

In simple language SMSI describes a phenomenon where the interaction between a metal catalyst and its oxide support becomes so strong—typically after high-temperature reduction—that it alters the metal's chemical and physical properties. : The metal's ability to adsorb gases like CO and H₂ decreases significantly. It has been associated with the support material may partially cover the metal particles, affecting their accessibility and results in reactions like ethane hydrogenolysis may decrease, while CO hydrogenation may increase

Strong metal-support interactions (SMSIs) have emerged as a significant and cutting-edge area of research in heterogeneous catalysis. These states play crucial roles in modifying the chemisorption properties, interfacial structure, and electronic characteristics of supported metals, thereby exerting a profound influence on the catalytic properties. The innovative designs and applications of new types of SMSI systems in catalytic chemistry are evolving. Their pivotal role in enhancing catalytic performance, selectivity, and stability in specific cases are interesting.. Particularly notable is the discovery of SMSI between active metals and metal carbides, which opens up a new era in the field of SMSI. Additionally, the strong interactions between atomically dispersed metals and supports require special attention.. . It is evident that SMSI modification has become a powerful tool for enhancing catalytic performance in various catalytic applications.

Strong metal-support interaction originally proposed by Tauster et al [1] conceptually refers to the altered activity of supported catalyst for hydrogenation reaction after heat treatment at 773 K. This concept has undergone many modifications with respect to the nature of the support (reducible or non-reducible) and also on the nature of the metal (their size and shape) and the method of loading the metal to the support. In today’s context it denoted the robust bonding between the dispersed metal atoms and the support material in a catalyst, which possibly facilitates the uniform dispersion of metal atoms and prevents their aggregation. This interaction is crucial for stabilizing isolated metal species and enhancing or altering the catalytic performance. The metal species have been designated nanoclusters, nanoparticles and single atom states and in these states the metallic species are isolated spatially and have unique electronic interactions with the support species. There are attempts to correlate with number of atoms, their sizes and shapes to the observed catalytic activity [2].

 Single atom species probably show a connection between homogeneous and heterogeneous catalysts, possessing well-defined molecular structures and high activity similar to homogeneous counterpart catalysts, along with the stability and ease of separation typical of heterogeneous catalysts. While single atom species result in high catalytic activity but mostly lead to aggregation. There are number of studies have found that nanocluster state or nanoparticle states possibly exhibit better catalytic activity due to interactions between single atoms and clusters or particles. Particle to cluster to single atom state of metals are not only differ in dimensions but also differ in the charge domain In shape and throw and these situations markedly affect the transformations promoted by these catalyst systems.   In these dimension scales, there is no general trend in the observed catalytic activity with decrease or increase in size, though it is presumed that decrease in size is favourable for catalysis, but in essence, the presence of active centres are identified to be the cause for the observed activity. This factor that is the number of active centres may be a size dependent. The catalytic centers in these configurations affect not only the number of active sites but also the chemical environment and electronic structure of the catalysts. It is necessary that one has to devise methodologies for fabricating the composite catalyst systems with these configurations of metal systems on supported catalysts..

Generally, the principal role of the support was initially ascribed to stabilization of the active component and/or increase in the metal dispersion and surface area.. However, it was soon realized that physicochemical interactions between the metal and the support can also influence catalytic performance through so-called carrier effects.

This state though manifests many remarkable catalytic properties with respect to hydrogen, the real reason for this altered activity as a result of higher temperature heat treatment is not clearly discernable but various models have been proposed. In this short write-up, some of these models are considered for evaluation purpose.

**(2) Encapsulation Model**

The model presumes that support phase migrates over the metallic site as a result of high temperature treatment. There are various points on which clarity are required.

1. Which type of supports are susceptible for encapsulation?
2. If the support encapsulates the metal what is the extent of encapsulation?
3. What types of alteration in properties that take place in the metal?

The support species which has higher migratory power are susceptible for encapsulation. This property depends on the reducibility of the support and also the ionic size of the species of the support. If the encapsulation layer thickness is unimolecular the effect on catalytic activity can be pronounced. The multilayer encapsulation may deactivate the catalytic activity. The unimolecular encapsulation of the support on metal sites depends on the surface energy of the metal species and also the support phase either oxide or molecular species like carbon. The difference in surface free energy between the two phases controls the extent of encapsulation and also the geometry of the encapsulation phase. Depending on the distribution surface free energy on metallic species and support phase controls the geometry of the encapsulation layer. Uniform wetting may influence the encapsulation layer to be a unimolecular layer on the metallic species. Depending on the distribution of surface free energy the encapsulation phase will be covering in patches or uniform or form different geometric shapes. [4-9]

The charge transfer between the metallic species and the encapsulating support phase is responsible for the observed altered catalytic activity. XPS binding energy value of core level has been commonly used to deduce the charge transfer between the metallic species and also the support. Cluster formation has been also proposed as the cause of the SMSI state. However, single atom, cluster and metallic particles all the three states have been identified in the SMSI state. There are many literature reports supporting this concept.{10,11]. It is not clear how this concept of encapsulation of metallic sites account for the observed altered catalytic activity There is still some uncertainty in the charge transfer concept and the extent of charge transfer in the SMSI state. It is essential to bring some clarity in this concept. The experimental evidence for charge transfer Is based on the value of the core level binding energy but this alteration can be due to the configuration change that takes place as a result of encapsulation of the support phase on metallic species. This is due to relaxation effect that will undergo changes as a result of encapsulation.

It is true the environment or coordination sphere of metallic particles can result in the altered activity of the metallic species. In addition, the heat treatment can result in aggregation of metallic species in the form of clusters or particle configuration (can also can even disentangle) and these changes can also account for the altered catalytic activity. It is true that encapsulation may take place as a result of high temperature treatment of supported catalyst systems. Aggregation and cluster formation may also take place but these effects can not be the reason for the altered catalytic activity. Encapsulation is dependent on the reducibility of the support and hence titania support systems is mainly associated with SMCI state Specific Geometric and electronic effects may result as a result of SMSI.

* SMSIs were first identified in the late 1970s, describing how suboxide supports encapsulate metal nanoparticles, enhancing resistance to sintering and degradation.
* Recent studies have expanded this concept to include interactions with metal carbides and atomically dispersed metals, revealing new mechanisms and effects.

**(3) Charge Transfer Model**

The localized charge transfer model was one of the first proposed to explain the strong metal-support interactions (SMSI) that occur upon high temperature reduction of metal catalysts dispersed on certain transition-metal-oxide supports [12,14]. This model accounts for the effects that are observed in SMSI state namely the alteration in the adsorption characteristics of hydrogen and CO is due to transfer of electrons from the cations of the reducible oxide support to the catalyst particles, thus changing their electron configuration.

The charge transfer from support to the metal species in the SMSI state and the observations of chemical shifts of core energy levels of metals {Photoemission measurements) in the SMSI state are rationalized in terms of a cluster model {the metal species constating of a number of metal atoms) consisting of surface species for the reduced support and metal. [15] Conventional view is that only reducible metal-oxide supports could induce a SMSI encapsulation state upon high-temperature treatments. High-temperature SMSI between platinum and sulfur-doped carbon supports, featuring charge transfer, suppression of H2/ CO adsorption, and support of encapsulation. Strong chemical interaction between platinum and sulfur atoms greatly suppresses platinum sintering at moderate temperatures, along with the subsequent formation of SMSI encapsulation structures at high temperatures .]16].

The strong metal-support interaction (SMSI) has long been studied in heterogonous catalysis on account of its importance in stabilizing active metals and tuning catalytic performance especially in Hydrogen or CO activation.. As a dynamic process taking place at the metal-support interface, the SMSI is closely related to the metal species surface properties which are usually affected by the size of metal nanoparticles (NPs). The discovery of a size effect on classical SMSI in Au/TiO2 catalyst where larger Au particles are more prone to be encapsulated than smaller ones. The catalytic performance of Au/TiO2 catalyst with uneven size distribution can be improved by selectively encapsulating the large Au NPs in a hydrogenation reaction.[17] .

With the increase of SMSI intensity, electrons are transferred from the TiOx capping layer to the Ru species. This effect facilitates the key steps of hydrogenation/desorption, while having little effect on the dehydrogenation and C–C cracking elementary reactions. As a result, the catalyst with higher hydrogenation capability prone to proceed hydrogenation and desorption step, thus suppressing cascade C–C cracking and avoiding the production of low value methane. The SMSI effect also enables the catalysts with superior stability, so it can also efficiently upcycle commercial polyolefins.[18].

The strong metal-support interaction (SMSI) in supported catalysts plays a dominant role in catalytic degradation, upgrading, and remanufacturing of environmental pollutants. Studies have shown that SMSI is crucial in supported catalysts' activity and stability. However, for redox reactions catalyzed in environmental catalysis, the enhancement mechanism of SMSI-induced oxygen vacabcy and electron transfer needs to be clarified. Additionally, the precise control of SMSI interface sites remains to be fully understood. Here we provide a systematic review of SMSI's catalytic mechanisms and control strategies in purifying gaseous pollutants, treating organic wastewater, and valorizing biomass solid waste  The adsorption and activation mechanisms of SMSI in redox reactions by examining interfacial electron transfer, interfacial oxygen vacancy, and interfacial acidic sites. Furthermore, we develop a precise regulation strategy of SMSI from systematical perspectives of interface effect, crystal facet effect, size effect, guest ion doping, and modification effect. Importantly, we point out the drawbacks and breakthrough directions for SMSI regulation in environmental catalysis, including partial encapsulation strategy, size optimization strategy, interface oxygen vacancy strategy, and multi-component strategy. This review article provides the potential applications of SMSI and offers guidance for its controlled regulation in environmental catalysis.

Strong metal–support interactions (SMSIs) are experiencing a renaissance in heterogeneous catalysis research, with exciting developments reshaping how we understand and design catalysts. Here's a snapshot of the current status:

* SMSIs influence charge transfer, particle morphology, and interfacial bonding, which are critical for catalytic activity, selectivity, and stability.
* Advanced characterization techniques (in situ/operando) are now used to probe these interactions, helping tailor catalyst architecture for specific reactions
* SMSIs are being harnessed to improve performance in reactions like CO oxidation, hydrogenation, and reforming.
* Novel systems such as Iridium on oxides and late transition metals on manganese or chromium oxides are predicted to exhibit strong SMSIs.

In short, SMSIs have evolved from a niche concept to a central pillar in catalyst engineering, driven by theoretical advances, computational tools, and experimental innovation. If you're exploring catalyst design or materials science, this is a frontier worth diving into. Want to explore specific applications or recent papers?

**(4) Cluster Model**

The cluster model for the Strong Metal-Support Interaction (SMSI) state is a conceptual and theoretical framework used to explain the electronic and structural changes that takes place when transition metals (typically Group VIII metals) are supported on reducible oxides like TiO, ZnO₂ and subjected to high-temperature reduction. As stted earlier, the hallmark of SMSI is the suppression of chemisorption for small molecules like CO and H₂. This is usually attributed to the encapsulation and electronic modification of the metal surface. : The model favors two-dimensional cluster formation over three-dimensional spherical morphologies. These clusters often exhibit "pill-box" shapes on the oxide surface.

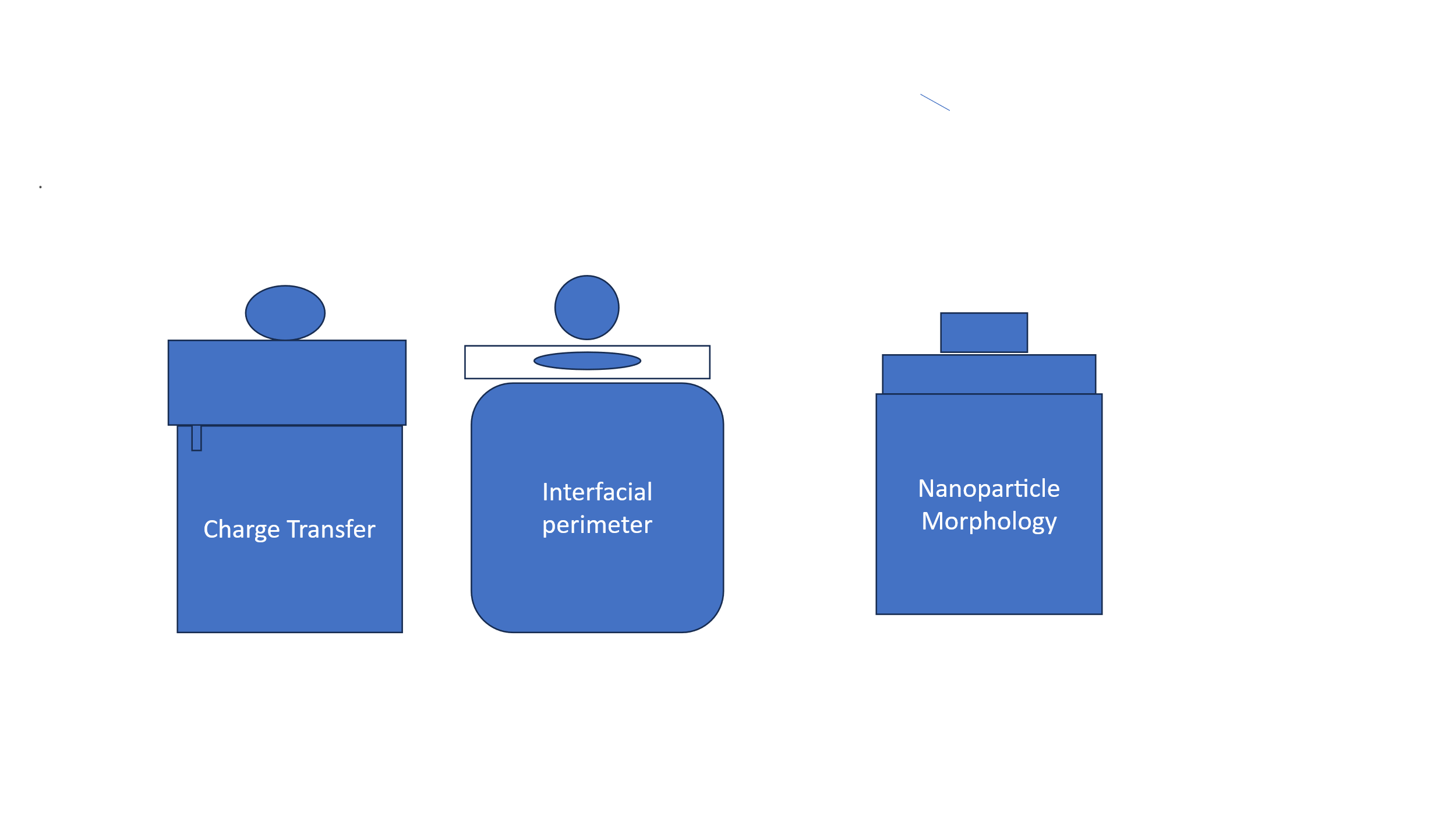
It is generally observed that the in SMSI state the metal particles take a pill-box configuration showing that the metal particles are taking two dimensional configuration and it is possible that the metal species takes a definite number of atoms aggregating to give rise to a cluster and this configuration facilitates encapsulation and charge transfer. []23,24]. It may be possible some aggregation or disintegration of the metal particles to give rise to a certain number of cluster which will exhibit surface properties suitable for the reaction under study.

(5) **Applications of SMSI state**

The Strong Metal–Support Interaction (SMSI) model plays a pivotal role in modern heterogeneous catalysis, offering a powerful framework for tuning catalyst performance.

Catalysis and Chemical Synthesis: SMSI can modulate the electronic and geometric structure of metal nanoparticles, improving their ability to catalyze reactions like CO₂ hydrogenation, ammonia synthesis, and hydrogenation of organic compounds. SMSI helps prevent sintering and deactivation of metal particles, extending catalyst lifespan in industrial processes. SMSI improves the efficiency of catalysts used in oxygen reduction reactions (ORR) and hydrogen evolution reactions (HER), which are critical for fuel cells and water splitting technologies. SMSI enhances charge transfer between metal and support, boosting solar-to-chemical energy conversion, such as in H₂O₂ production via oxygen reduction. SMSI-based catalysts are used in automotive exhaust treatment and industrial emission control, helping break down NOₓ, CO, and hydrocarbons more effectively.. SMSI enables selective oxidation and reduction reactions with minimal byproducts, supporting sustainable chemical manufacturing. SMSI allows for fine-tuning of reaction pathways, which is valuable in producing high-purity chemicals and pharmaceuticals with fewer purification steps.

Pictorially these models are shown in Fig.1.

Fig.1.Pictorial representation of the models of SMSI state 

**(6) Various forms of SMSI**

The other forms of SMSI are termed The C-SMSI was limited to the interaction between Group VIII metals and reducible oxides, which resulted in its application in electrocatalysis being limited**.** The C-SMSI occurs between metal and reducible metal oxide under a reducing atmosphere, where electrons transfer from the support to the loaded metal. The characteristics of strong metal support interaction under oxidation conditions are opposite those of C-SMSI, the electrons of the O-SMSI transfer from the metal to the support**.** The induction of A-SMSI can be achieved through adsorption-mediated induction or different gas inductionThe degree of encapsulation and electron transfer of the encapsulation layer can be controlled by changing the gas composition or proportion.. W et chemical method to induce SMSI in solution has become another feasible method. (WS-SMSI). This method makes use of mild conditions and hence limited encapsulation. The forms of SMSI are pictorially shown in Fig.2.

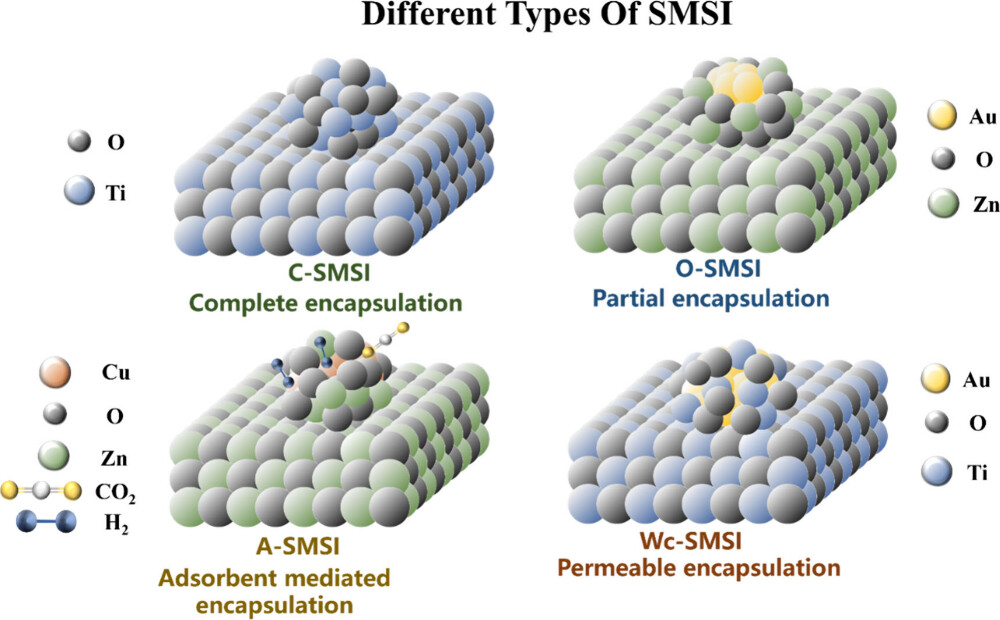


Fig.2. Different forms of SMSI Reproduced from (*Inorg. Chem.* 2025, 64, 10, 4713-4748)

The forms are different in the extent of encpasulation and also the extent charge transfer and direction, the reduction in surface energy and changes (increase) in entropy are the prime factors distinguishing the different forms of SMSI.

**(7) Conclusion**

Physical attributes like encapsulation or charge transfer may be taking plce but the altered activity is due to intrinsic changes that take place in the metal particle is probably the cause. This may be in the segregation of cluster sizes or the geometrical disposition of the cluster metallic particle. This type of creation of new altered active sites may account for the altered activity, However, these type of alternate views for SMSI state us necessary since the existing situation appears to be an art or magic. More theoretical models have to be developed to understand what takes place in the metallic particle as a result of heat treatment. It is hoped that the situation will develop soon so that considerable progress will take place to account for the not only altered activity but also enhanced activity in hydrogenation reactions. Another aspect of SMSI state is speciric to hydrogen and carbon monoxide but its universality has yet to be established.

The models proposed for SMSI state are aimed to explain the effects observed as a result of SMSI state but what really takes place in the SMSI state has not yet been fully and clearly outlined. This situation has to be improved soon if one wants to exploit the benefits of this state fully. Catalytic activity alteration is one aspect but understanding the state is essential to exploit this state fully and also repeatedly.

Strong metal–support interactions (SMSIs) have thus emerged as a significant and cutting-edge area of research in heterogeneous catalysis. They play crucial roles in modifying the chemisorption properties, interfacial structure, and electronic characteristics of supported metals, creation of new active sites, (mainly at the periphery of metal and support) altering the activity of the existing sites thereby exerting a profound influence on the catalytic properties. New innovative designs and applications of new types of SMSI systems in catalytic chemistry and brings out their pivotal role in enhancing catalytic performance, selectivity, and stability in many cases. Particularly notable is the discovery of SMSI between active metals and metal carbides, which opens up a new era in the field of SMSI. Additionally, the strong interactions between atomically dispersed metals and supports are important for catalysis. The chemical nature of SMSI and its underlying catalytic mechanisms are interesting.. It is evident that SMSI modification has become a powerful tool for enhancing catalytic performance in various catalytic applications**.**

Developing a fundamental theory for SMSI state has been challenging because of the intricate interfaces. However, in a limited sense it can be recognized in ‎metal-metal and metal-oxygen interactions. This concept has been applied to late-transition metal catalysts, metal-metal interactions dominated the oxide support effects [27].

The changes observed in SMSI state serve to enhance the catalyst’s activity, stability, and reaction selectivity. In recent years, a multitude of novel SMSI types and induction methods including oxidized SMSI (O-SMSI), adsorbent-mediated SMSI (A-SMSI), and wet chemically induced SMSI (Wc-SMSI) have been introdued. It is recognized that SMSI significantly contributes to enhancing catalyst stability, altering reaction selectivity, and increasing catalytic activity. Extensive application of SMSI in the electrocatalysis of hydrogen evolution reaction (HER), oxygen evolution reaction (OER), oxygen reduction reaction (ORR), and carbon dioxide reduction reaction (CO2RR) have also been shown [30].

Strong metal–support interaction (SMSI) could facilitate the formation of multicomponent alloy by establishing a tunnel of oxygen vacancy for metal atom transport under low reduction temperature (400–600 °C), which exemplifies the holistic design of multicomponent alloy catalysts without deactivating supports.[31].

Metal nanoparticles stabilized on a support material catalyse many major industrial reactions. Metal-support interactions in these nanomaterials can have a substantial influence on the catalysis, making metal-support interaction modulation one of the few tools able to enhance catalytic performance. A systematic rationalization of the field is still lacking due to the great diversity in catalysts, reactions and modification strategies. Metal-support interaction is most impactful for metal nanoparticles smaller than four nano-meters.[32].

Pt and Pt based alloy catalysts have been shown to encapsulate or migrate in CdS nanorods [33]. Optimizing support oxides to control oxygen vacancies enhances the catalytic performance of CO2 hydrogenation to methanol.[34]. The effects of SMSI on the catalytic activity, selectivity and stability of various reaction systems, such as heterogeneous catalysis and [electrocatalysis](https://www.sciencedirect.com/topics/materials-science/electrocatalysis) are examined extensively [35]. Strong metal-support interaction (SMSI) can be normally induced by the surface free energy differences between metal nanoparticles and supports[36].

The strong metal-support interaction (SMSI) has associated with stabilizing active metals and tuning catalytic performance. SMSI is affected by the size of metal nanoparticles (NPs). It has been shown that larger Au particles are more prone to be encapsulated than smaller ones [37].. Surface energy minimization has been advocated as the reason for the altered activity in SMSI state [38].It haas been reported that a sputter−anneal procedure that transfers Pt nanoclusters on TiO2(110)-(1 × 1) from their almost inert SMSI state to a catalytically active and thermally stable one for CO oxidation. The procedure prevents the encapsulation of the Pt clusters by a thin, reduced titania layer, which usually forms by high-temperature treatment of Pt/TiO2 and is known to be responsible for the catalytic passivity of the metal clusters[39]. SMSI effect is characterized by strongly bound adsorbates (HCO*x*) on reducible oxide supports (TiO2 and Nb2O5) that induce oxygen-vacancy formation in the support and cause HCO*x*-functionalized encapsulation of Rh nanoparticles by the support [40]. The encapsulation layer is permeable to reactants, stable under the reaction conditions and strongly influences the catalytic properties of Rh, which enables rational and dynamic tuning of CO2-reduction selectivity.

It may bepossible

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