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

**B. Viswanathan, Department of Chemistry, Indian Institute of Technology, Madras, Chennai 600 036**

**1.Introduction**

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.

**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.

**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.

**References**

[1] S.J. Tauster, S.G. Fung and R.L. Garten, Strong metal support interactions Group 8 noble metals supported on titanium oxide, J. Am. Chem. Soc., **100**, 170-175 (1978).

[2] Bingkun Huang , Zelin Wu , Hongyu Zhou , Xinhao Wang , Yang Liu ,Heng Zhe, Zhoikun Xiong and Be Lei, The structure-performance relationships in active center size-dependent Fenton-like catalysis: From nanoparticles to single atoms, Applied Catalysis B Environment and Energy,**355,** 15 October 2024, 124157

[3] [Hailian Tang](https://www.science.org/doi/10.1126/sciadv.1700231#con1) , [Yang Su](https://www.science.org/doi/10.1126/sciadv.1700231#con2), [Bingsen Zhang](https://www.science.org/doi/10.1126/sciadv.1700231#con3), [Adam F. Lee](https://www.science.org/doi/10.1126/sciadv.1700231#con4) , [Mark A. Isaacs](https://www.science.org/doi/10.1126/sciadv.1700231#con5), [Karen Wilson](https://www.science.org/doi/10.1126/sciadv.1700231#con6) [Lin Li](https://www.science.org/doi/10.1126/sciadv.1700231#con7), [Y,uegong Ren](https://www.science.org/doi/10.1126/sciadv.1700231" \l "con8), [Jiahui Huang](https://www.science.org/doi/10.1126/sciadv.1700231#con9) and [Tao Zhang](https://www.science.org/doi/10.1126/sciadv.1700231#con16), Classical strong metal–support interactions between gold nanoparticles and titanium dioxide, Science Advances, [Vol. 3, No. 10](https://www.science.org/toc/sciadv/3/10).(2017).

[4] 1. Y. Gao, Y. Liang, S. A. Chambers, Thermal stability and the role of oxygen vacancy defects in strong metal support interaction—Pt on Nb-doped TiO2(100). Surf. Sci. 365, 638–648 (1996).

[5] L. Zhang, R. Persaud, T. E. Madey, Ultrathin metal films on a metal oxide surface: Growth of Au on TiO2 (110). Phys. Rev. B 56, 10549–10557 (1997).

[6] D. W. Goodman, “Catalytically active Au on Titania:” Yet another example of a strong metal support interaction (SMSI)? Catal. Lett. 99,1–4 (2005).

[7] A. G. Shastri, A. K. Datye, J. Schwank, Gold-titania interactions: Temperature dependence of surface area and crystallinity of TiO2 andgolddispersion. J. Catal. 87, 265–275 (1984).

[8] R. Meyer, C. Lemire, S. K. Shaikhutdinov, H.-J. Freund, Surface chemistry of catalysis by gold. Gold Bull. 37,72–124 (2004).

[9] Q. Fu, T. Wagner, S. Olliges, H.-D. Carstanjen, Metal–oxide interfacial reactions: Encapsulation of Pd on TiO2 (110). J. Phys. Chem. B. 109, 944–951 (2005).

[10] H. R. Sadeghi, V. E. Henrich, SMSI in Rh/TiO2 model catalysts: Evidence for oxide migration. J. Catal. 87, 279–282 (1984). 11. S. J. Tauster, Strong metal-support interactions. Acc. Chem. Res. 20, 389–394 (1987).

[11]. S. Roberts, R. J. Gorte, A study of the migration and stability of titania on a model Rh catalyst. J. Catal. 124, 553–556 (1990).

[12] Victor E. Henrich, The Validity of Cluster Models of Localized Charge Transfer in SMSI’, Journal of Catalysis, 88, 5 19-522 (1984).

[14] B. Viswanathan, K. Tanaka and I, Toyoshima, Cluster Model and Charge Transfer in a Strong Metal-Support Interaction (SMSI) State, Lanmuir, 1986, 2, 113-116.