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Tuning/exploiting Strong Metal-Support Interaction (SMSI) in Heterogeneous Catalysis

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ABSTRACT

Interactions between metals and supports are of fundamental interest in heterogeneous catalysis. The electronic, geometric and bifunctional effects originating from Strong Metal-Support Interactions (SMSI) that are responsible for the catalyst's activity, selectivity, and stability are key factors that determine performance. Research into SMSI is fast-growing with many revolutionary systems being developed to enhance our understanding of its nature and effects.

This review starts with a brief overview of heterogeneous catalysis and SMSI; then three major mechanisms involving electronic, geometric and bifunctional effects are summarized to introduce the fundamental concepts, recent progress and disagreement remained. Subsequently, advanced analytical techniques are introduced as contemporary approaches to the investigation and understanding of SMSI. In addition, the effects of SMSI on the catalytic activity, selectivity and stability of various reaction systems, such as heterogeneous catalysis and electrocatalysis are examined. Additionally, a brief review of various protocols used for the manipulation of interactions between metals and supports is given. Lastly, the future of SMSI with respect to further developments and ongoing challenging issues is addressed.

1. Introduction

The application of catalytic technologies, on a major scale in the 20th century, to a huge number of industrial synthetic processes - ranging from petrochemicals to pharmaceuticals, as well as to diverse applications, such as, the treatment of waste, the sensing of crucial physiological metabolites and the generation of green energy, has undoubtedly been a major driving force underlying both social change and economic progress [1].

Given the now ubiquitous presence of catalysts within the industrial base of the developed economies, it should be of no great surprise to find catalysts occupying an ever more important role in the energy economy. The drive for ever increasing efficiency in energy harvesting, storage and conversion; especially with respect to the development of fuel cells, solar cells, and bio-energy, has highlighted the need for ever more versatile and robust functional materials. To anyone who has ever paid more than a cursory glance at the history of chemical reactions in the energy economy the central importance played by catalysts will be obvious.

Recently a wide range of supports, in addition to those involving the oxides of transition or non-transition metals, have been investigated and shown to have the potential to augment the catalytic potential of platinum and other catalytically active metals. The catalyst support should ideally embody such properties as mechanical strength, a resistance to dissolution or disintegration and the ability to act as a carrier upon which the catalytic particles can be distributed as uniformly as possible – thus maximizing the surface area exposed to the reactants. Thus, supports can be formed as powders, granules, pellets, wires, or as extruded structures for specific applications.

The interaction between metals and oxide supports, so-called metal-support interactions, are of great importance in heterogeneous catalysis [2,3] and electrocatalysis [4]. The term strong metal-support interaction (SMSI) was first used by Tauster et al., in 1978 [5]. They discovered that the chemisorption of H_2 and CO of metal clusters on TiO_2 would decrease significantly, when the material was chemically reduced at high temperatures. Now, the term of SMSI has been generally used to summarize changes in

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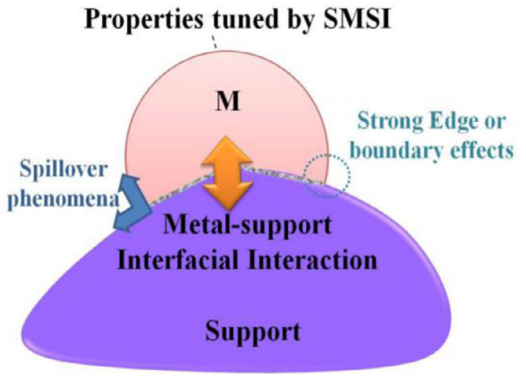

Scheme 1. A model of a supported metal particle, illustrating the effects of metal-support interfacial interactions.

catalytic activity and selectivity when group VIII metals supported on reducible oxides are treated by a high-temperature reduction process [3,6]. SMSI commonly appears at the metal-support interface where the support is reducible, e.g. with TiO_2, CeO_2, Nb_2O_5, [7] and V_2O_3 [5,6,8]. SMSI plays a critical role in determining catalytic activity and stability. Gold particles supported on metal oxides, such as TiO2, Fe2O3, and CeO2 possess significant oxidation activity when compared to unsupported gold particles [9]. SMSI was originally explained as an electron transfer between the support and the metal [10], or by the formation of intermediate phases [11]. Current thinking with respect to the fundamental concepts underlying strong metal-support interactions additionally attaches importance to interfacial and transport phenomena, together with charge redistribution during metal-support interface formation. SMSI gives rise to three major effects (electronic, geometric and bifunctional), as shown in Scheme 1. The change in the electronic properties of the metal catalyst originates from the strong interactions between the cluster and the oxide support [12,13]. The geometric effect originates from the physical covering of a thin layer of a reducible oxide species blocking active catalytic sites on the metal's surface. [3,14–23] The bifunctional effect provides dual active sites at the perimeter between the metal and the support leading to significantly improved catalytic activity/selectivity. The reaction species can migrate or spillover either from metal or support to the boundary or edge where the chemical reactions occur. Recognition of the importance of SMSI has attracted many researchers in diverse heterogeneous catalytic applications such as chemical synthesis [24] water splitting [25] and environmental engineering [26–30].

In heterogeneous catalysis, the size of the catalytic materials has to be in the nanosized region in order to have the highest surface area upon which the reaction will take place. With such nanosized catalysts, formed as supported nanoparticles, the interactions between the catalytic nanoparticles and the support are significantly enhanced. Understanding and 'tuning' that interaction is crucial for enhancing the performance and durability of catalytic materials. Much progress in the understanding of metal-support interaction has been made thanks to modern surface science techniques [31,32] and advanced computational modeling methods [33,34]. A useful representative model system consists of an ultra-thin layer of metal or nanometer scale metal cluster supported on well-defined single crystal surfaces. By utilizing this model we can simplify a variety of issues related to interface interactions [35]. Such a computational simulation also contributes to our understanding of many aspects of the nature of metal/oxide interfaces [33].

This review, focused on Strong Metal-Support Interactions (SMSI) in heterogeneous catalysis, commences by examining the current state of knowledge with regard to the electronic, geometric and bifunctional effects that underlie the activity, selectivity and stability of heterogeneous catalysts. Prior to examining contemporary practical applications of SMSI in various reactions such as CO oxidation, methanol oxidation, oxygen reduction reaction, hydrogenation, and in applications such as fuel cells and heterogeneous catalysts, consideration will be given to material characterization by various techniques, including spectroscopic techniques, such as X-ray Photoelectron Spectroscopy (XPS), X-ray Absorption Spectroscopy (XAS), Electron Energy Loss Spectroscopy (EELS), and microscopic techniques, such as Transmission Electron Microscopy (TEM), and Scanning Probe Microscopy (SPM). The remainder of the paper looks to the future of SMSI, specifically by examining the way we can manipulate catalytic properties by synthesizing rationally designed materials; such design considerations embody the totality of our current understanding of the electronic/structural nature of the catalytic materials. In fact, the incorporation of computation into an experimental design will play a pivotal role not only in enabling us to understand reaction mechanisms, but also in the search for new catalysts. Theoretical computations provide us with deep insights; especially with respect to reaction mechanisms, cluster growth and interfacial characteristics that cannot be gleaned from experimentation due to limitations imposed by instrumental sensitivity or extreme conditions. However, it is regrettable that the paper cannot include a more rigorous treatment of theoretical investigation approaches due to the article length.

2. Mechanism of SMSI

The excellent review article by Fu and Wagner [31] provides an extensive discussion focusing on the thermodynamics and kinetics of interfacial phenomena that occur at metal-support interfaces. Interfacial phenomena involving chemical reactions, transport phenomena or charge redistribution during metal-support interface formation define the underlying fundamental concepts of strong metal-support interactions. The properties of metals and their supports are affected by strong metal-support interactions; this is especially the case for nanomaterials, where their properties are dramatically changed due to nanoscale effects. It is of great interest and importance to understand such effects, so that novel materials can be designed for industrial applications. SMSI effects are key factors that determine the performance of heterogeneous catalysts and nano-devices [31]. The present review article mainly focuses the effects that result from the formation of strong interactions between metals and supports. Three major effects, namely (1) electronic, (2) geometric, and (3) bifunctional ones, will be addressed in the following sub-sections.

2.1. Electronic effect

The strong metal-support interaction induces an electronic effect [5,36] which has been known in catalysis for over 50 years, since the work of Schwab [2,37] and Solymosi [38]. Interfacial contact between a metal and a support can result in charge redistribution at the interface. The electronic interactions are governed by fundamental principles, e.g. energy minimization and the continuity of the electric potential in a solid [39]. When a metal is in contact with a support, depending on the degree of interaction, either weak or strong metal-support interactions (WMSI or SMSI) can occur. These phenomena are often invoked to explain catalytic effects resulting from electron transfer between metals and supports. It has been a matter of interest to modify the metal-adsorbate bond and further alter the catalytic activity by controlling such electron transfer.

Electron transfers always occur at reactive interfaces, where already existing chemical bonds are broken and new ones are

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