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# Designing a new generation of catalysts: Water gas shift reaction example

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ABSTRACT

In the present work, we briefly review the main conclusions harvested until now in our previous works regarding the WGS reaction together with new results, examples and key ideas for designing WGS catalysts. Most of the ideas and general statements included in the present work may be also very useful for designing catalysts for other reactions that require the presence and combination of metals and oxides. Particularly relevant is the description of the nature, properties and future implications of the nano-mixed-oxide phase "naturally" generated at the interface of some systems which modifies and activates the whole catalytic process. Co-supporting metal and reducible-oxide nanoparticles on another oxide-support in systems with a strong oxide–oxide interaction opens the door to a new family of highly active catalysts suitable for reactions such as water gas shift, CO oxidation or methanol synthesis, among others.

## 1. Introduction

The so-called water gas shift (WGS) reaction, $CO + H_2O \rightarrow CO_2 + H_2$, is one of the main steps in the production of $H_2$ for fuel cells [1–3]. Therefore, it is related to the finding and improvement of clean and renewable sources of energy [3,4]. The reaction needs to be promoted by temperature and a convenient catalyst. Metals alone have been shown to be poor WGS catalysts [5–7]. This comes from the high barrier observed for $H_2O$ dissociation, both as flat surface, rough surface or even as nanoparticles (NPs) (see Table 1). However, from theoretical calculations it has been shown that the other steps and transitions states involved in the whole WGS reaction are usually exothermic with low activation barriers on metals [6]. On the other hand, reducible oxides alone as $CeO_2$ or $TiO_2$ are able to dissociate $H_2O$ readily when they are partially reduced and consequently $Ce^{3+}$ or $Ti^{3+}$ species are present in the system [1,8]. For instance, the barrier for $H_2O$ dissociation at reduced $TiO_2$ has been computed to be as low as 0.35 eV [9]. Nevertheless, the reducible oxides alone are not active at all for the WGS reaction. The reason comes from the highly stable intermediates (formates, carbonates, etc.) they usually form in a mixture of $H_2O$ and CO [9]. Those intermediates are so stable that it is very difficult for the system to evolve to products and the reaction stops. These two behaviors are schematized in Fig. 1.

What it is needed is a mild way, which it could be called "soft reaction", where the energies of the intermediates are neither so high nor so low, but just in a smooth reaction pathway (Fig. 1). The ideal reaction pathway would be a continuous descending way between reactants and products in an exothermic reaction. Since metals are high-energy-way and oxides are low-energy-way for the WGS reaction, one could expect the combination of both could work well. That is the case. In a nice paper, Rodriguez and coworkers [1] showed that although neither Au(1 1 1) nor $CeO_2$(1 1 1) are active at all for the WGS reaction, deposited small nanoparticles of cerium oxide on the Au(1 1 1) surface show a good catalytic activity. The same fact was observed for $TiO_2$ nanoparticles on Au(1 1 1). Moreover, they found that the reduction of the oxide (the presence of $Ce^{3+}$ species in the case of $CeO_2$) is critical for the water dissociation step and, at the same time, they stated that the metal phase has to be exposed to reactants along with the reduced oxide. It could be said then, that the WGS catalyst is a bifunctional catalyst in which the role of the reduced oxide is dissociate water and the role of the metal is to adsorb CO and to form less stable intermediates at the interface. This work opened the door to many interesting questions on the WGS reaction mechanism and above all it constituted a solid understanding base for searching, improving and optimizing new highly active WGS catalysts.

The subsequent research efforts were focused then on answering main questions as:

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**Table 1**
Activation barriers and reaction energies for the adsorbed-water dissociation process ($H_2O_{(ads)} \rightarrow H_{(ads)} + OH_{(ads)}$) on different metal surfaces and nanoparticles (NP).

| | Activation barrier (eV) | Reaction energy (eV) |
|---|---|---|
| Au(1 1 1)[a] | 1.95 | 1.59 |
| Au(1 0 0)[a] | 1.53 | 0.74 |
| Au(NP)[a] | 1.29 | 0.6 |
| Cu(1 1 1)[b] | 1.36 | 0.01 |
| Cu(1 0 0)[a] | 1.13 | 0.39 |
| Cu(NP)[a] | 0.93 | −0.21 |

[a] Data taken from Ref. [6,8].
[b] Data taken from Ref. [7].

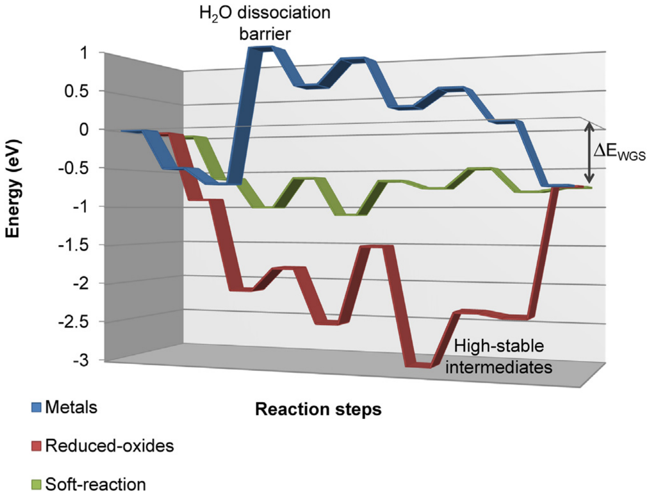

**Fig. 1.** WGS reaction profiles. Usual reaction profiles (including intermediates and transition states) for bare metals and reduced oxides. A hypothetical "soft-reaction" profile, which leads the reaction through an energy path neither so-high nor so-low but just a middle smooth pathway, is also depicted.

- There are two configurations to combine oxides and metals: (1) the *conventional* configuration consisting of metal nanoparticles supported on an oxide support, and (2) the so-called *inverse* configuration in which oxide nanoparticles are supported on a metal support (see Fig. 2). Which configuration will report a higher activity and why?
- As bifunctional catalyst, there are two roles in the catalytic process: (1) the reduced oxide phase has to be able to dissociate water and (2) the metal must adsorb CO and lead the reaction to the formation of less stable weakly-bound intermediates at the interface. Which role is more important for the WGS catalytic activity? The answer of this question is critical for the optimization of the catalyst, since it will allow us to know if we should foster the oxide phase over the metal or vice versa.
- Finally, and related to those questions: is there a general way or strategy to improve the catalytic activity by optimizing at the same time both phases, i.e., the oxide and the metal phases?

In the present work, we review briefly the main conclusions harvested until now in our previous works regarding the WGS reaction together with new results, examples and key ideas for designing WGS catalysts. Most of the ideas and general statements included in the present work may be also very useful for designing catalysts for other reactions that require the presence and combination of metals and oxides, for instance methanol synthesis or CO oxidation reactions. Particularly relevant is the description of the nature, properties and future implications of the nano-mixed-oxide phase "naturally" generated at the interface of some systems which modifies and activates the whole catalytic process.

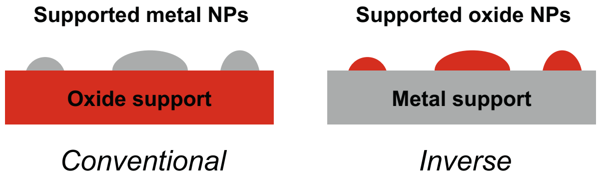

**Fig. 2.** Conventional vs. inverse catalyst configuration. "NPs" stands for nanoparticles.

## 2. Oxide–metal interaction in the inverse catalysts

As mentioned before, there are two configurations for combining an oxide and a metal to form a catalyst: conventional and inverse configurations (Fig. 2). In the conventional catalyst the role of the metal is fostered, as the metal is dispersed in nanoparticles, adopting then its most active configuration. It has been shown in many ways, in many systems and in many works that metal nanoparticles are more active than flat or rough surfaces. For example, in Ref. [12] we showed that effect in the catalytic activity of copper for the WGS reaction. A clear decreasing of the apparent activation energy is seen when passing from flat-packed surface as Cu(1 1 1) to more opened and lower coordinated surface Cu(1 0 0), and further lowering is observed when passing from surface to nanoparticles as in Cu/ZnO, where Cu nanoparticles are supported on ZnO. A number of factors are involved in the explanation of the higher activity of the nanoparticles over the surfaces, some of them are: (i) nanosize effects, higher ratio of corners, vertex, edges, and structural defects, which usually are more reactive due to the undercoordination of the atoms occupying those positions. (ii) Also the so-called "fluxionality" of the metal nanoparticles, i.e. their ability to get, in an almost energetically costless way, structurally deformed conformations, allowing a better interaction with the adsorbed species, accommodating dynamically the structure for a stronger bond (obviously in a surface those structural relaxations are much more constrained by the periodicity and packing of the atoms in the ordered crystal than in a nanoparticle). (iii) A further aspect is the higher probability of charge transfer processes coming from the interaction with the support. In contrast, in the same conventional configuration, the oxide phase is in its less active conformation since it is set to be a bulk-support flat surface.

On the other hand, in the inverse configuration, the role of the oxide is fostered over the role of the metal, since now the oxide is supported as nanoparticles on a bulk-metal flat surface. In the case of the supported oxides, we would like to add a new remarkable factor to the factors mentioned before for explaining the higher activity of the nanoparticles over the bulk-surfaces: it has been shown than the reducibility of the oxide increases when decreasing the size of the oxide particle [10,11], being the reducibility of the oxide critical for the dissociation of water in the WGS reaction.

As an example, we show here the results for $CeO_x$/Cu(1 1 1) vs. Cu/$CeO_2$(1 1 1). In Ref. [12], we showed that WGS reaction activity is significantly higher in $CeO_x$/Cu(1 1 1) than in Cu/$CeO_2$(1 1 1). Therefore, from experimental observations, fostering the role of the oxide phase seems to be more important than fostering the role of the metal. It would be then a great mistake to consider the oxide as a simple support in the conventional catalytic systems. The oxide may play a role even more important than the role of the metal in the whole catalytic process. Now, the question is why that happens. We performed state-of-the-art DFT-based calculations for answering this point.

It was experimentally observed by STM images that in the $CeO_x$/Cu(1 1 1) system, very small $CeO_x$ particles (2–5 nm in size) together with large ones (30–50 nm in size, triangular shape,