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Embedded Metal Particles : A way to active and stable catalysts

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Hydrogen plays a key role in our daily life, as it is extensively used as feed stock in many important industrial processes. Nowadays enormous quantities of H₂ are used for ammonia/fertilizers production and to purify oil from sulphur and nitrogen through hydrodesulphurization (HDS) and hydrodenitrogenation (HDN) processes. In addition, it is used abundantly in the methanol synthesis, synthetic fuel production via Fisher-Tropsch process, hydrogenation reactions, margarine production, etc. Furthermore, there are immense expectations for its possible key role as energy vector of the future, since its use in fuel cells can lead to very high energy conversion efficiency with virtually zero pollution emissions.¹

Currently, hydrogen is predominantly produced by reforming of methane under rather severe working conditions.² The progressive depletion and increasing cost of fossil fuel requires the development of alternative and sustainable hydrogen production processes. Additionally, logistical limitations, namely its storage and transportation, promote also the R&D of small and medium in-situ processes for the production of hydrogen. In this context, heterogeneous photocatalysis by harvesting sunlight for splitting water is the ideal substitute for the conventional methods of hydrogen production.

It is well known that the efficiency of a catalyst is directly proportional to its surface area. For this reason, many of the heterogeneous catalysts, used in industry today, consist of one or several catalytically active component(s) in the form of very small particles (typically in the size range of 1-100 nm) deposited on a suitable support (e.g. oxide), a highly porous and thermostable material with a high surface area and proper mechanical strength. The use of nanoparticles results in a large contact area between the active sites of the catalyst and surrounding gas or liquid phase.

The extremely small size of the particles maximizes surface area exposed to the reactant, allowing more reactions to occur. However, thermal stability of these nanomaterials is limited by their critical sizes; the smaller the crystallite size, the lower thermal stability. The main purpose of using a support is to achieve an optimal dispersion of the catalytically active component(s) and to stabilize it (them) against sintering and hence to increase the catalyst life. Furthermore, in several reactions, the support is not inert and the overall process is actually a combination of two catalytic contributions: that of active component(s) and that of the support.

A general problem of metal nanoparticles is their tendency to undergo agglomeration, which increases their particle size, and therefore, dramatically reduces the catalytic activity.^{3,4} Two general strategies have been developed to stabilize the particle size of the metal, namely, supporting the metal nanoparticles on suitable solid surfaces or by using suitable ligands.⁵⁻¹² However, while the use of dendrimers,¹³ surfactants¹⁴ or polymers¹⁵⁻¹⁷ as metal nanoparticle stabilizers is well documented in the literature, significantly lower information is reported on the use of more thermally resistant inorganic porous networks.

It has been developed by our group a simple and low cost strategy for the synthesis of efficient and stable embedded Rh-based catalysts (Figure 1) for Methane Partial Oxidation (MPO) and Ethanol Steam Reforming (ESR).¹⁸⁻²⁰ The method offers the possibility to modulate the nature of the support and its texture, the inclusion of extra components (e.g. ceria-based mixed oxides as promoters) in the catalyst formulation, thereby leading a strong flexibility to the approach. The catalysts can be obtained by co-precipitation method composed by two steps. In the first step a stable suspension of protected metal nanoparticles are obtained according to the method reported in the literature by Schulz and coworkers.^{14,21} The metal particles are prepared in the presence of a highly water-soluble ionic surfactant which is able, due to its nature, to modulate the particle size and to prevent their aggregation. Modifying parameters like pH, temperature and surfactant concentration, it is possible to tune the metal particle sizes.¹⁸ Moreover, the role of surfactant is also to control the encapsulation of pre-formed metal particles in the second part of the synthesis. During this step the growth of the porous oxide layers around metal nanoparticles also takes place. In order to remove organic materials, post-synthesis treatments are required leading to final catalyst.

The embedded catalyst synthesized in this way presents higher thermal stability respect to the traditional catalyst obtained by conventional impregnation.

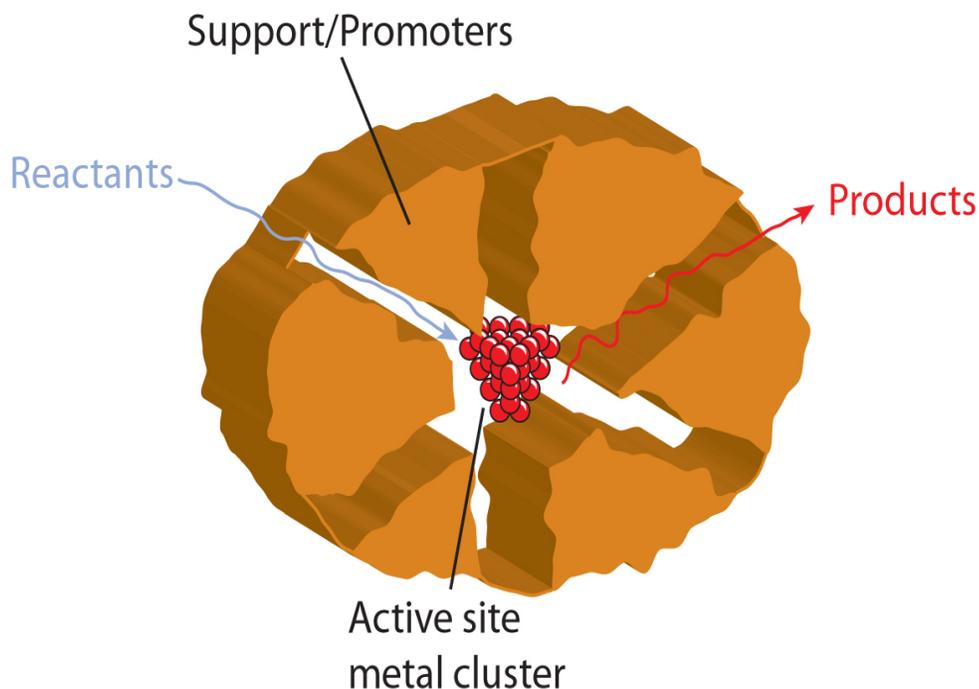


Figure (1) : representative picture of an embedded catalyst.

In the case of MPO, run-up experiments demonstrated that the reaction follow a Combustion-Reforming pathway, in which CH_4 is completely oxidized in the first part of the catalytic bed, while the remaining CH_4 is converted to syngas reacting with CO_2 and H_2O in the rest of the catalytic bed.

The stability of the catalyst was tested at 750 °C, the lower temperature at which the complete conversion of CH₄ is reached. The activity of the embedded catalyst remained stable for at least 70 hours, while a reference catalyst (prepared by incipient wetness impregnation using a similar Al₂O₃ support) started to deactivate immediately. In the case of embedded catalyst, an oxidative treatment at high temperature completely restored the initial activity and stability. H₂ chemisorption measurements evidenced that the exposed Rh surface area is slightly reduced after the aging under MPO conditions while it is essentially restored by the oxidative treatment. This indicated that the partial deactivation observed is essentially related to the deposition of coke on the active phase. On the contrary, in the case of the impregnated sample, the deactivation is deeper and the Rh surface area is completely excluded to the probe gas, also after oxidative treatment: in this case, the deactivation is mainly attributable to the metal sintering.

The production of H₂ through ESR was investigated as a possible way to produce syngas starting from renewable materials. In this case, the high activity of Rh-based catalysts was attributed to the ability of Rh to dissociate C – C bond. The embedded catalysts developed demonstrated a high activity through syngas production. An appropriate design of the protective oxide allowed the production of catalytic system with a particular long lifetime. In fact, changing the oxidic matrix from Al₂O₃ to a nanocomposite Ce_xZr_{1-x}O₂-Al₂O₃, the dehydrogenation of ethanol to acetaldehyde with respect to its dehydration to ethylene was promoted at low temperature. Both the products (CH₃CHO or CH₂CH₂) were subjected to steam reforming to syngas at higher temperature, but in the case of the dehydration-reforming pathway the amount of carbonaceous deposits was higher with respect to that deposited by the dehydrogenation-reforming pathway, suggesting that the introduction of the Ce_xZr_{1-x}O₂ component provided reactive oxygen useful to deactivation prevention. Also in this case, the Rh exposed surface area was essentially unperturbed after different aging treatments, validating the benefits introduced by the appropriate synthetic methodology.

More recently, we highlighted the key role of the intimate contact between Cu/CuOx nanoparticles and TiO₂ in order to maximize the photocatalytic hydrogen production from methanol/water solution.²² The comparison of the performances of Cu/CuOx nanoparticles, with similar average dimension, impregnated on or embedded into a porous TiO₂ clearly demonstrated that the Cu/CuOx nanoparticles embedded in a structural skeleton can enhance the working potential of TiO₂ leading to improved photocatalytic efficiency for hydrogen production.

Cu-based TiO₂ were prepared both by classical “wet impregnation” of preformed titania and by water-in-oil micro-emulsion (ME) synthesis, with the aim of obtaining Cu-based nanoparticles starting from protected Cu ones. In all cases the Cu loading was 2.5% w/w.

The comparison of photocatalytic hydrogen production on the investigated systems showed that both the pure TiO₂ polymorphs are complete unable to produce hydrogen under the experimental conditions adopted. Notably, the embedded systems exhibited significant higher yield of hydrogen production with respect to the impregnated Cu/TiO₂. The superior activity can be interpreted on the bases of combination of positive effects :

- (i) high dispersion of the active Cu/CuOx species,
- (ii) large presence of anatase phase and
- (iii) efficient metal-support interaction

The fact that embedded Cu particles serve as the “core” for the electron transfer processes, initiated in the surrounding TiO₂ particles with the absorption of light ($E > E_g$), for hydrogen production along with the centre for charge carrier recombination inhibition process. Secondly, in the case of

embedded system, the Cu phase, being deeply surrounded by the porous TiO₂, is protected against the adsorption of poisoning species, generated by photocatalytic oxidation of methanol and water in the aqueous methanol system.

Some other encouraging results came from Pd- and Au-based catalysts for WGS and PROX reactions (unpublished results). Also in this case, embedding approaches have been used to entrap preformed metal nanoparticles inside CeO₂ porous matrices, leading to the obtainment of rather but especially thermally stable catalysts.

In the case of Pd, the microemulsion technique has been used with a novel strategy. As CeO₂ precursor, Ce alkoxides soluble in non-polar solvents have been prepared. Pd nanoparticles have been prepared into a microemulsion by reducing Pd²⁺ cations inside the water droplets using hydrazine or sodium borohydride. Then, Ce alkoxides have been added into the oily phase of the microemulsion and they hydrolyzed when in contact with the water droplets containing Pd nanoparticles. In this way, a Ce(OH)_x layer have been formed around the particles, leading to their inclusion into the support in the final calcined material. The properties of the as-prepared materials have been compared to those prepared by classical impregnation methods. Despite a lower activity in the WGS, mainly due to the low surface area they possess, these materials showed superior thermal stability when subjected to harsh reaction conditions if compared to impregnated Pd/CeO₂ catalysts of similar composition.

Summarizing, the kinetic stabilization of metastable materials containing or representing the active sites is a fundamental factor to prepare stable catalysts for different applications. One of the key answer to this question is the design of new synthetic approaches which are able to incorporate metal nanoparticles into an “open shell” of an oxide that can limit the sintering of the particles at high temperature while preventing a total occlusion of the particles, and consequently favoring the accessibility of the catalytic sites to the reactants. In our opinion the approach of metal nanoparticles embedded in porous oxides will be widely adopted for the preparation of the innovative catalyst of the 21st century.

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