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Additional Information

## Heterogeneous catalysis: Understanding the fundamentals for catalyst design

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Taking the chemoselective hydrogenation of substituted nitroaromatics as a base case, it will be shown that it is possible to design improved and new catalysts by attacking the problem in a multidisciplinary way. By combining molecular modeling with in situ operando spectroscopy, and with micro-kinetic and isotopic studies, it is possible to determine how and where on the catalysts the reactant molecules interact. Then, materials synthesis methods can be applied to prepare catalysts with the desired surface active sites and their selective interaction with the reactants.

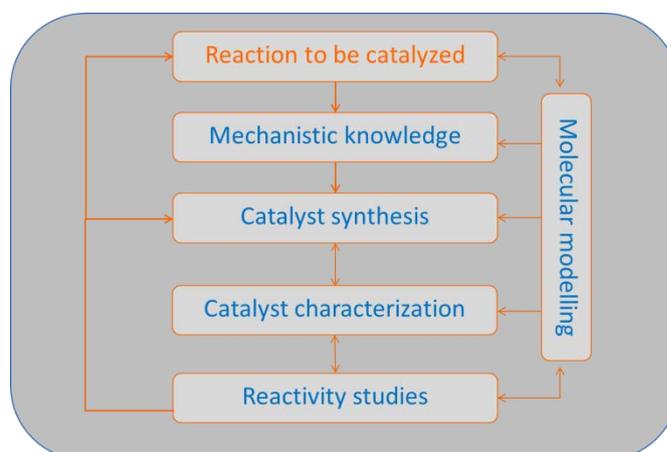
### Introduction

The final objectives in heterogeneous catalysis is to reach catalysts by design. This could be done by increasing our arsenal of fundamental knowledge on the molecular interactions at the solid-gas or solid-liquid interface, and the synthesis techniques required for preparation of the material that will act as catalyst (1). The development of new spectroscopic techniques able to work under reaction conditions should bring key knowledge on surface homogeneity and surface dynamics, especially when interacting with reactants. Indeed, the determination of the active sites and reaction mechanism under dynamic conditions, i.e. under realistic working conditions, can strongly help to establishing structure-reactivity selectivity relationship. This will strongly be helped by operando spectroscopy for investigating the dynamic structure of solid catalyst under real working conditions, and the simultaneous measurement of activity and selectivity. It is clear that extrapolation of the results obtained by following the operando methodology, it is only possible if the reactor catalyst activation and catalytic reactor conditions are analogous to those used under realistic operation. In this respect, several reviews have been published (2). It is then clear that for in deep knowledge of the catalytic phenomena, combination of material synthesis, multitask surface characterization techniques, molecular simulation and micro kinetic studies will be required. From these combined efforts, not only our scientific knowledge will increase, but will be able to design better solid catalysts for improving existing process and for opening new reaction avenues. In our studies, after selecting the reaction to be

catalyzed, the reaction mechanism is considered first in order to postulate the potential active sites. We will show that this could be achieved by combining micro kinetic and mechanistic studies, with molecular modeling and in situ spectroscopy studies, preferentially under working conditions. Finally, through the materials synthesis techniques, catalysts with well defined single or multisites will be generated. Following this strategy, it should be possible, not only to explain and understand how a given catalyst works, but to design the next catalyst generation.

### Results and discussion

In our studies in heterogeneous catalysis, regardless if we work with zeolites, structured inorganic, hybrid organic-inorganic materials, metal nanoparticles or multifunctional catalysts, we attempt to select the reaction to be studied not only because of its intrinsic chemical interest, but also with the objective to apply the knowledge acquired to solve an industrially relevant problem. In other words, we have always attempted to combine generation of scientific knowledge and potential application. For achieving this, the methodology given in Figure 1 has been applied and will be illustrated here for the development of chemoselective hydrogenation catalysts based on uni and bimetallic nanoparticles and clusters.



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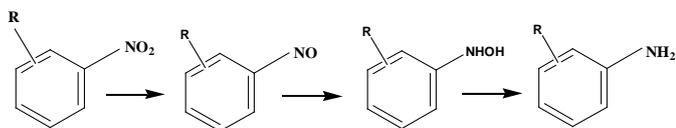
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Figure 1. Methodology Followed for Heterogeneous Catalytic Studies

**The reaction**

Amines are important building blocks in inorganic synthesis and are widely used industrially. They can be obtained by hydrogenation of  $-NO_2$  groups into the corresponding amines. This, in principle, is not a difficult process and, for instance, aniline is successfully produced industrially from nitrobenzene, with  $H_2$  and different metal catalysts. However, the nitro group could be difficult to be selectively reduced with  $H_2$  when other reducible groups are present in the same molecule and have to be retained in the final product. This will be the case when the nitro compounds have to be hydrogenated in the presence of olefin, alkyne, carbonyl or nitrile groups. To tackle this problem, and owing to its industrial interest, researchers from Ciba-Geigi (5) have carried out the chemoselective hydrogenation of  $-NO_2$  in the presence of olefins and alkyne groups, with supported Pt catalysts. Since supported Pt was not selective, those authors modify the metal with PbO or  $H_3PO_4$  and added vanadium and iron salts into the solution to avoid the accumulation of partially reduced nitro compounds. In fact, as presented by Haber (6), the reaction mechanism for the reduction of nitro compounds follows the sequence presented below:



Then, with the Pt catalyst described above, the potentially explosive hydroxylamine compound was accumulated and vanadium and iron were required to decrease its concentration. While the results obtained are interesting, it is clear that the above catalytic system was not optimum from an environmental point of view and a more elegant catalyst should be developed.

**The catalyst**

Chemical steps in a catalytic reaction involve reactant adsorption and activation, followed by the surface reaction. In the case of chemo, regio and enantioselective hydrogenations, the adsorption step can be determinant for the final selectivity. In the case of substituted nitrobenzene, and more specifically nitrostyrene, a potentially chemoselective catalyst could be achieved with a solid that adsorbs the nitrostyrene selectively through the nitro group instead of adsorbing the molecule of nitrostyrene flat on the surface (Figure 2).

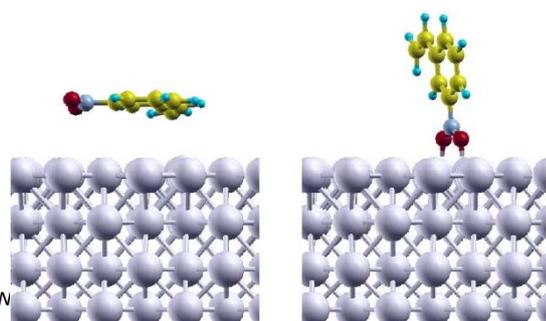


Figure 2. Adsorption modes of nitrostyrene on the catalyst metal surface

Since non selective catalysts such as Pt, Pd or Ni, adsorb nitrostyrene flat on the surface, and gold is a good material for adsorbing nitrogen oxides while it is a poor olefin hydrogenation catalyst, we thought on using nanoparticulated gold for carrying out the selective reduction of nitrostyrene. Results in Table 1 show (7) that while gold on  $TiO_2$  was chemoselective, neither Pt or Pd were. Then, the question was if the selectivity of gold catalyst was because of the selective adsorption of nitrostyrene through the nitro group or it was due to differences in the intrinsic rate of hydrogenation of the nitro and olefinic group on the gold catalyst.

Substrate	Catalysts	% Metal (Mol)	T (°C)	P (bar)	Time (hours)	Conversion (%)	Selectivity (5)
3-Nitrostyrene	Au/TiO <sub>2</sub>	0.23	120	9	6.00	98.5	95.9
	Pd/C	0.11	120	9	0.03	99.0	0.0
	Pt/C	0.12	120	9	0.03	96.7	2.9
4-Nitrobenzaldehyde	Au-Pt/TiO <sub>2</sub>	0.31	120	9	0.02	93.0	1.8
	Au/TiO <sub>2</sub>	1.14	100	10	1.25	99.0	96.8
	Pd/C	0.35	100	10	0.03	92.0	29.8
	Pt/C	0.38	100	10	0.03	96.7	68.6

Table 1. Nitrostyrene reduction on supported metal catalysts.

**Understanding the interactions at the solid-liquid, solid-gas interface**

To understand the mechanism of action of the catalyst, styrene, nitrobenzene and a 50% mixture of nitrobenzene and styrene were reacted on the Au/TiO<sub>2</sub> catalyst. The results presented in Table 2 clearly demonstrate the key role played by the reactant selective adsorption. Indeed, the higher intrinsic hydrogenation activity of Au/TiO<sub>2</sub> for nitrobenzene, cannot explain the very high chemoselectivity observed in Table 1. Meanwhile, when the 50% mixture was reacted, results in Table 2 show a very strong decrease in the rate of hydrogenation of the olefinic group, while there is not effect on the hydrogenation of the nitro group.

Feeding (%mol)		TOF (h <sup>-1</sup> )	
8.5	0	160	0
0	8.5	0	360
4.25	4.25	16	405

Table 2. Competitive hydrogenation of substituted nitroaromatics on Au/TiO<sub>2</sub> catalyst.

The question then was: where and how does specific adsorption through the nitro group occur on the catalyst?. To answer the question, molecular modeling of nitrostyrene adsorption on well defined Au metal faces, surface unsaturated atoms and gold nanoparticles was carried out, using periodic DFT calculations with VASP code PW 91 functional – PAW pseudopotential,  $\Gamma$  point, a cut-off of 400-500eV and Au clusters and NPs in a 20x20x20 Å box (8). The results showed no adsorption of nitrostyrene on extended Au (111) and Au (100) surfaces and some preferential adsorption of C=C on defective surfaces and on isolated Au<sub>38</sub> NP (see Figure 3).

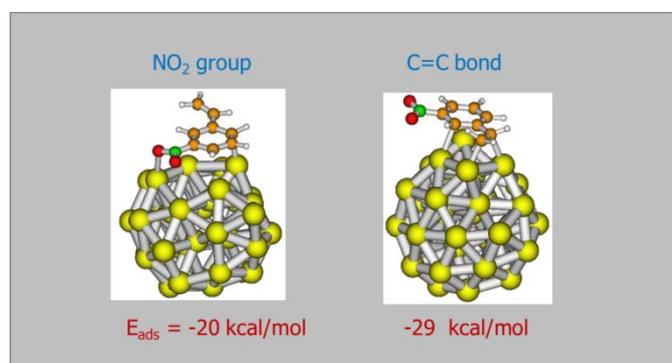


Figure 3. DFT results of nitrostyrene adsorbed on gold nanoparticles

The answer from the molecular modeling was that specific adsorption on gold could not be the responsible for the observed chemoselectivity. With these bases, an experimental study was carried out, and IR spectroscopy of adsorbed nitrobenzene, styrene and nitrobenzene + styrene on Au/SiO<sub>2</sub> and Au Ti/O<sub>2</sub> showed that the key adsorption of nitrostyrene was not taken place on gold but on TiO<sub>2</sub>. Moreover, nitrostyrene adsorbed gave two adsorption bands, one at 1526 and another at 1520 cm<sup>-1</sup> that can be associated with  $\nu$  (NO<sub>2</sub>)- TiO<sub>2</sub> and  $\nu$  (NO<sub>2</sub>)-Au-TiO<sub>2</sub> (gold-TiO<sub>2</sub> interface) (Figure 4).

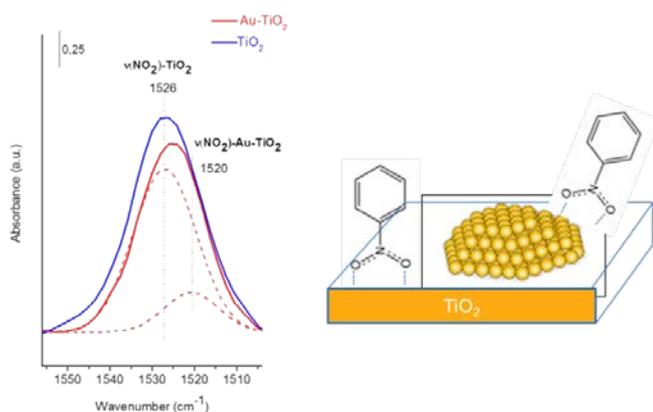


Figure 4. Nitrobenzene adsorption on Au/TiO<sub>2</sub> catalyst followed by IR spectroscopy

Then, when the reaction was performed in situ, the IR clearly showed that the nitrostyrene adsorbed at the interface was reacting, while that adsorbed on the Ti was a spectator (Figure 5).

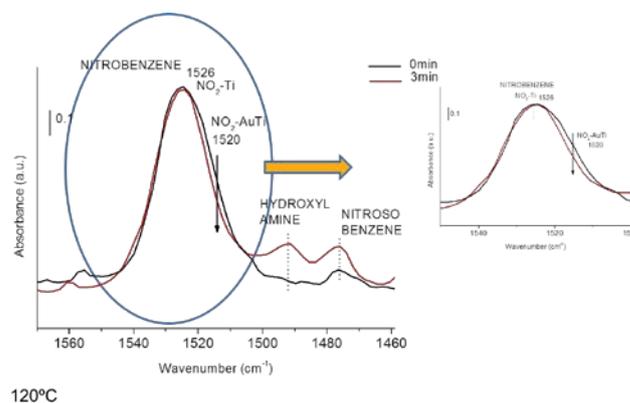


Figure 5 Nitrobenzene hydrogenation on Au/TiO<sub>2</sub> Catalyst IR spectroscopy

At this point and combining kinetics, in situ spectroscopy and molecular modeling, we know that there is indeed a preferential adsorption of nitrostyrene by the NO<sub>2</sub> group at the gold-Titania interface. Furthermore one could assume in a first approximation that H<sub>2</sub> will be dissociated on gold. With the knowledge already acquired and with the objective of designing a better catalyst, one should find what is the reaction controlling step and which are the catalytic active sites involved. To do that, different surface kinetic models were built assuming that the controlling step was nitrostyrene adsorption, H<sub>2</sub> dissociation, surface reaction between dissociated H<sub>2</sub> and activated nitrostyrene on the same or in different sites. Kinetic experiments indicated that H<sub>2</sub> dissociation was the controlling step, being this confirmed by H<sub>2</sub>/D<sub>2</sub> isotopic exchange.

#### Improving the catalysts through fundamental knowledge

It was now clear that if H<sub>2</sub> dissociation is the controlling step, the design of an improved catalyst should increase the rate of H<sub>2</sub> dissociation. This could be achieved by: a) increasing the number of active sites responsible for such activation, b) increasing the intrinsic H<sub>2</sub> dissociation activity by site modification, c) by increasing both.

The dissociation of H<sub>2</sub> was studied theoretically on different gold surfaces and supported gold nanoparticles. It was found the unsaturated gold atoms were responsible for such dissociation (9). This is in agreement with the conclusion reached previously by Hammer and Norskov (10). Taking the above into account, it would then appear that more sites active for H<sub>2</sub> dissociation should be achieved when decreasing the crystallite size of the metal nanoparticles, since the fraction of gold atoms located at corners

and borders will be larger. Indeed, higher catalyst activity was obtained for Au/TiO<sub>2</sub> catalysts with smaller gold nanoparticles. The second way to increase catalyst activity is by increasing the intrinsic activity of the H<sub>2</sub> dissociation sites, without losing the specific adsorption properties. Along that direction, it is clear that Pt metal is more active than gold for H<sub>2</sub> dissociation but it is not chemoselective. However, we could accomplish both conditions, i.e., faster H<sub>2</sub> dissociation and selective nitrostyrene adsorption, by introducing small amounts of Pt on the gold catalyst. The Pt should be at the level of a few atoms per each gold nanoparticle to avoid a dominant role of Pt. Indeed, when this was done, no activation energy for H<sub>2</sub> dissociation was observed, which is in contrast with the existence of an activation energy (though low) for H<sub>2</sub> dissociation on the pure gold nanoparticles (Figure 6). Moreover, nitrostyrene was still adsorbed through the nitro groups at the interface of gold-TiO<sub>2</sub> in the bimetallic particles (Figure 7) (11).

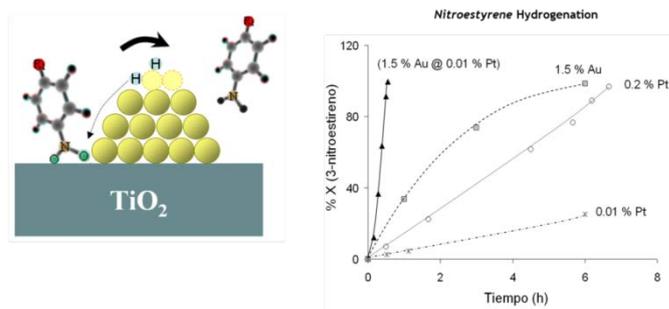


Figure 8. Hydrogenation of nitrostyrene on Au@Pt catalyst.

### Transforming non selective into selective catalyst from the knowledge acquired

If a selective catalyst requires avoiding the adsorption of the nitrostyrene flat on the catalyst surface, but at the metal/TiO<sub>2</sub> interface, this could be achieved if one prepares Pt and Ni catalysts with very small metal domains, i.e. only exposing low surface coordinated sites. This could occur if one decorates Pt or Ni crystallite with Titania by calcination of Pt or Ni supported on TiO<sub>2</sub> at 450°C (12). When this is done, the results in Table 3 (13) show good activities and selectivities.

Catalytic System	Reduction Temperature (°C)	% X	% Sa	% Sb	% Sc	% Sd
1.5% Au/TiO <sub>2</sub>	---	98.5	95.9	0.0	3.9	0.2
0.2% Pt/TiO <sub>2</sub>	450	95.1	93.1	0.1	6.8	n.d.
5% Ni/TiO <sub>2</sub>	450	93.0	90.2	0.2	7.3	2.3

Table 3. Hydrogenation of 3-Nitrostyrene on different metal with their surface decorated with TiO<sub>2</sub>. a: 3-aminostyrene; b: nitroethylbenzene; c: 3 ethylanilina; d: hydroxylamina derivatives.

Recently, decoration of Pt nanoparticles by ZnO in Pt/ZnO catalysts have shown a similar increase in catalyst selectivity (14). High activity and selectivity for hydrogenation of nitrostyrene derivatives have also been obtained by preparing silver-cerium oxide core-shell nanoparticles (15).

As a result of all the above, it is possible to achieve a wide scope of substituted anilines synthesized by hydrogenation of the corresponding nitro compounds with metal nanoparticles supported on TiO<sub>2</sub>. Moreover, by having such chemoselectivity, one can perform one pot cascade reactions starting with nitro compounds and reacting the amines formed with molecules bearing alkyne, carbonyl, alkene, nitrile groups etc (Figure 9).

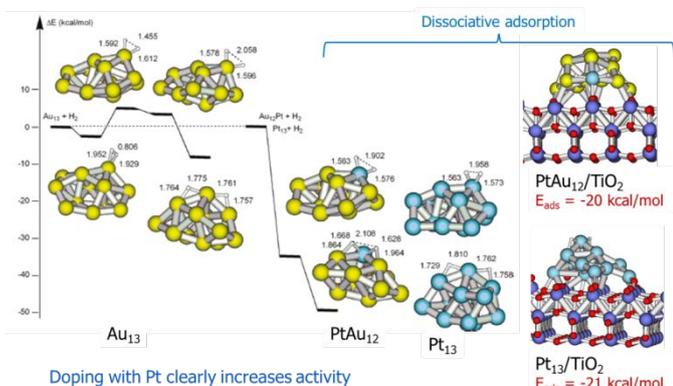


Figure 6. Reaction Coordinate for Hydrogenation of nitrostyrene: role of doping gold with Pt.

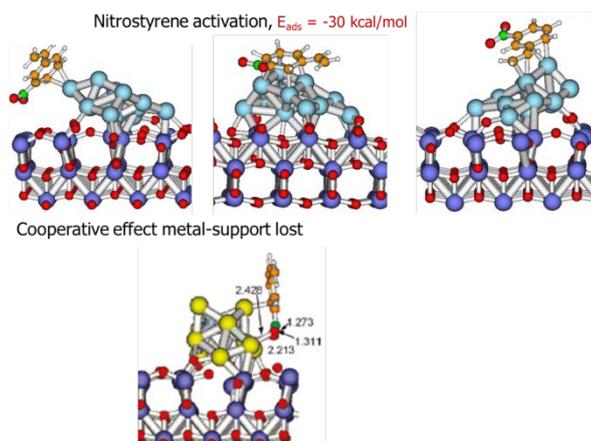


Figure 7. Hydrogenation of Styrene by doping gold with Pt.

Catalytic results confirm the above calculations and the catalytic activity of Au/TiO<sub>2</sub> was strongly increased, while preserving selectivity when 100 ppm of Pt is introduced in the catalyst (Figure 8).

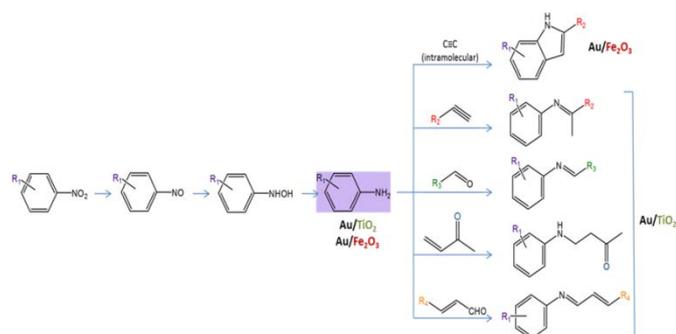


Figure 9. Cascade reactions starting with nitroanilines

In this way, imines, secondary amines, nitrones,  $\beta$ -amino carbonyls can be produced in high conversions and selectivities (16-21).

By combining the selective metals with other acid and base catalytic functions, we were also able to perform the one pot synthesis of 3-methyl 2-pyrrolidones (22), 1,5-benzodiazepines from nitroaromatic compounds, quinoxalines from dinitroaromatics and glycols (23) and 2'-aminochalcones from 2-nitroacetophenones and benzaldehydes.

#### Chemoselective hydrogenations with non noble metals catalysts

Considering the cost and limited availability of noble metals, it is important to prepare non-noble metal catalysts for chemoselective hydrogenation reactions. In fact, modified non-noble metals can present comparable properties to noble metals in photocatalysis, electrocatalysis and heterogeneous catalysis (24-27).

Non noble metals such as  $\text{CoO}_x$  and  $\text{Fe}_2\text{O}_3$  on N doped carbon materials have been successfully used for the hydrogenation of nitroarenes (28-29). These catalysts give good chemoselectivity, though they required to work at 50 bar of  $\text{H}_2$  instead of the 10 bar required by gold. Furthermore, the role of the layer carbon component on final catalytic performance is still unknown. It may protect metal NPs, but it may also block accessibility of substrates to the metal NPs. One hypothesis on the role of carbon in the above catalyst (30-32) was that the hydrogenation may occur on the surface of carbon layers.

In our case, we have prepared cobalt-carbon nanoparticles ( $\text{Co@C}$ NPs) by reduction of Co-EDTA complex in  $\text{H}_2$ . The morphology of  $\text{Co@C}$ NPs consists of nanodispersed metal NPs ranging from 20 to 150 nm (Figure 10). The CoNPs are covered by a few carbon layers, and HRTEM images indicate that the CoNPs are formed by a core-shell structure with metal Co at the core,  $\text{CoO}_x$  at the shell and the outside carbon layers.

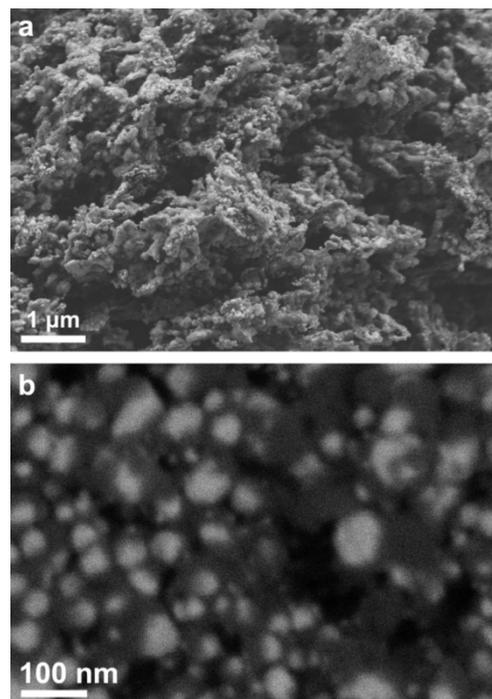


Figure 10. Field-emission scanning electron microscopy (FESEM) images of  $\text{Co@C}$  NPs obtained by SE2 detector (a) and ESB detector (b). In Fig. a, Co NPs are surrounded by foam-like carbon and those Co NPs with particle size ranging from 20 to 100 nm can be seen in Fig. b

The above preparation allows having stable CoNPs avoiding agglomeration and deep oxidation without necessity of capping with organic ligands. The carbon layers present in our preparation allow to store the CoNPs for long times without observable morphological changes. Oxidation occurs only at the surface and the NPs can be reduced to metallic Co under very mild conditions (7 bar  $\text{H}_2$ ,  $120^\circ\text{C}$ ). This is a clear advantage with respect to other preparation methods reported that require calcinations at  $800^\circ\text{C}$ . The  $\text{Co@C}$ NPs prepared from Co and EDTA are active and chemoselective for the hydrogenation of nitrostyrene, working at very mild reaction conditions. In fact, 93% selectivity to 3-aminostyrene can be obtained at 95% conversion working at 7 bar of  $\text{H}_2$  and  $120^\circ\text{C}$ , instead of the 50 bar  $\text{H}_2$  required with previous catalysts. No leaching was observed during the reaction and catalyst recyclability was good.

We have extended this type of catalysts to bimetallic materials, and the preparation method avoids metal segregation, and excellent metals dispersion can be achieved.

The reactant interaction at the interphase was studied by in situ IR spectroscopy, and the results obtained indicate that metallic Co is responsible for the preferential adsorption of the nitro group, while the olefinic group will be preferentially adsorbed in the presence of cobalt oxide.

This work opens the possibility to prepare stable multiatomic catalyst nanoparticles and to control the adsorption properties towards different reactants.

## Conclusions

We have attempted to show that improving the knowledge of the molecular interactions at the catalyst surface is key to understand the catalytic phenomena. That includes the nature of the solid surface under reaction conditions, the nature of the active sites at work, and their interaction (adsorption-reactivity) with reactants. The study of such complex systems require the combination of different techniques that make “visible” the structures and interactions. They include HRTEM better in the presence of reactant, and in situ spectroscopic techniques working at reaction conditions. Molecular modeling allows to understand the molecular interaction, helps to the imagination and directs into prediction. Last, but not least, microkinetic studies, together with spectroscopy work for detection of intermediates, help to deep into the reaction mechanism. By following that multitask methodology it should be possible to go from understanding to prediction and to achieve improved or even completely new type of catalysts.

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