Catalysis Today xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Combined theoretical and spectroscopic mechanistic studies for improving activity and selectivity in heterogeneous catalysis

Mercedes Boronat*, Patricia Concepción

Instituto de Tecnología Química, Universitat Politècnica de València-Consejo Superior de Investigaciones Científicas (UPV-CSIC), Av. de los Naranjos s/n, 46022, Valencia, Spain

ARTICLE INFO

Article history:
Received 25 September 2016
Received in revised form
21 November 2016
Accepted 25 November 2016
Available online xxx

Keywords:
DFT
IR spectroscopy
Kinetics
Catalyst design
Hydrogenation
C—C bond forming reactions

ABSTRACT

By combining theoretical modelling, *in situ* spectroscopy and kinetic studies it is possible to understand, at the molecular level, the role that the different types of active centres co-existing on real heterogeneous catalysts play on each elementary step of the global reaction mechanism. The fundamental knowledge acquired by means of this multi-disciplinary approach in two selected reactions, the chemoselective hydrogenation of substituted nitroaromatics and the Sonogashira coupling between aryl halides and alkynes, is applied to direct the rational synthesis of more efficient industrial catalysts based on noble metal particles supported on metal oxides.

1. Introduction

In the actual context towards a sustainable development, catalysis is the main tool available to design cleaner and more efficient chemical processes. This means, on one hand, to reduce the use of energy by decreasing the temperature at which reactions happen and allowing to work under milder reaction conditions, and on the other hand, to optimize the use of raw materials and minimize the generation of waste and undesired by-products. In general terms, and until not long ago, catalyst development and optimization strongly relied on an empirical "trial and error" approach, with little knowledge about the chemical nature of the catalytically active sites. Within this approach, combinatory chemistry achieved a lot of interests in the nineties. In the last years, fundamental understanding of the reaction mechanisms at the molecular level, identification of the nature of the active centres involved in all elementary steps, and knowledge on how to tune their reactivity, has achieved great impact in the field of catalysis, allowing a rational design and synthesis of industrial catalysts. So far, many studies have focused on simple model systems whose catalytic properties can be easily and systematically investigated by means of theoretical calculations and surface science techniques. Conclusions are then translated to the design of real catalysts, thus bridging the gap between model and real systems. However, the complexity of most real heterogeneous catalysts, which usually consist of metal and/or metal oxide particles of varying diameter and morphology, supported on inorganic matrixes that modify their electronic properties, and containing a distribution of active centres not completely equivalent, makes this task difficult and not always successful. A different way to rationally design highly efficient industrial catalysts relies on the study of model systems which are sufficiently complex to mimic the real catalysts through a multi-disciplinary approach, by combining macro-kinetics, spectroscopic techniques and computational methods.

Theoretical modelling plays a key role in the study of the mechanism of the target reaction, including determination of the geometry, stability and electronic properties of reactant and intermediate species interacting with different active sites present on the catalyst, as well as determination of transition states and activation energy barriers for all elementary steps constituting the global process. By combining theoretical modelling with kinetic studies it is possible to identify, at the molecular level, the active sites that catalyse both the desired steps and the undesired side-reactions of the mechanism, providing useful hints to guide the rational synthesis of the most selective catalyst for each reaction. On the other

---

* Corresponding author.
E-mail addresses: boronat@itq.upv.es (M. Boronat), pconcepc@upvnet.upv.es (P. Concepción).

http://dx.doi.org/10.1016/j.cattod.2016.11.048
0920-5861/

Please cite this article in press as: M. Boronat, P. Concepción, Combined theoretical and spectroscopic mechanistic studies for improving activity and selectivity in heterogeneous catalysis, Catal. Today (2016), http://dx.doi.org/10.1016/j.cattod.2016.11.048

hand, the experimental identification of the active centres present in the synthesized materials, and the study of the evolution of the reactant and intermediates species adsorbed on the catalyst, are usually based on the use of spectroscopic tools.

In the last years, many spectroscopic techniques with high resolution have been developed which deliver precise information on the composition, topology, and reactivity of solid surfaces with down to atomic resolution. These include surface methods, such as X-ray photoelectron (XPS), Auger (AES) and Infrared (IR) spectroscopies, or surface microscopy methods, which at the current state of development enable element-specific atomic level imaging of the investigated surfaces, and other more bulk-like techniques like Raman spectroscopy, UV–vis, X-ray diffraction (XRD), etc. Moreover, many of these techniques can be performed under operando conditions, thus allowing to investigate not only the evolution of the adsorbed intermediate species, but also the stability of the active centres and the possible generation of new active sites under reaction conditions. All this information coupled with macro-kinetic studies is used to optimize the synthesis of new catalysts and/or to modify the technical design of the catalytic process.

In this paper we present two selected examples, studied in our group, on how fundamental knowledge gained through combination of Density Functional Theory (DFT) calculations, IR spectroscopy and kinetic studies has directed the synthesis of new catalysts for industrially relevant processes. Specifically we focus on the selective hydrogenation of substituted nitroaromatics and on C—C bond forming reactions.

2. Selective hydrogenation of substituted nitroaromatics

Aromatic amines are valuable intermediates in the industrial production of pharmaceuticals, agrochemicals, pigments and dyes, and they are usually obtained by catalytic hydrogenation of the corresponding nitroaromatic compounds. The reduction of nitrobenzene and other simple nitrocompounds with hydrogen is easily carried out with commercial catalysts based on Pd, Pt or Ni. But the selective reduction of a nitro group in molecules containing other reducible groups such as carbonyl, cyano, or C=C double bonds is more challenging, and it usually requires the use of a stoichiometric amount of reducing agent or the addition of soluble metals and other modifiers [1,2]. The discovery that gold nanoparticles supported on TiO_2 or Fe_2O_3 selectively catalyse the hydrogenation of the nitro group in substituted nitroaromatics under mild reaction conditions [3] opened the possibility to develop an environmentally benign process for this relevant reaction [4]. Selectivities larger than 95% to the desired aromatic amines were reported for the hydrogenation of 3-nitrostyrene, 4-nitrobenzaldehyde or 4-nitrobenzonitrile using Au/TiO_2 catalyst. Unfortunately, the hydrogenation activity of Au/TiO_2 is too low for industrial application, and research was devoted to improve activity while preserving its excellent chemo selectivity.

2.1. Understanding chemo selectivity of Au/TiO_2

To design an efficient catalyst or to improve the performance of an existing one it is necessary/desirable to have a detailed knowledge of the mechanism of the target reaction and of the active centres participating in each elementary step. To establish the reaction pathway in the case of Au/TiO_2 catalyst and the rate determining step of the process, a series of kinetic studies were performed in our group in combination with FTIR and isotopic H/D exchange experiments [5,6]. It was first demonstrated that on Au/TiO_2 a hydroxylamine intermediate is rapidly formed by successive hydrogenation steps, and slowly reduced to the final product, aniline [5]. Going one step further, a detailed kinetic study of nitrobenzene hydrogenation using the Hougen-Watson formalism combined with H/D isotopic studies allowed to determine that the rate determining step of the global process is the dissociation of H_2 on gold, [6] and that attempts to improve the activity of Au/TiO_2 should focus on increasing the concentration of the active sites where H_2 is split.

As regards selectivity, macro-kinetic studies of nitrobenzene and styrene hydrogenation over Pt/TiO_2, Au/SiO_2 and Au/TiO_2 catalysts showed a faster hydrogenation of the C=C bond in Pt/TiO_2 and Au/SiO_2, and a reverse order of reactivity on Au/TiO_2, a trend which is greatly enhanced when the nitro and C=C groups are competing for the active centres. It was proposed, based on the kinetic study, that the high chemo selectivity of Au/TiO_2 was mainly related to a preferential adsorption of nitrostyrene through the nitro group, a hypothesis confirmed by FTIR spectroscopy and DFT calculations [7]. No adsorption of nitrobenzene could be detected over Au/SiO_2 by FTIR spectroscopy, indicating a weak interaction of the nitro group with gold nanoparticles. On the contrary, the spectra corresponding to nitrobenzene and styrene co-adsorption on TiO_2 and Au/TiO_2 showed exclusively the bands associated to nitrobenzene (see Fig. 1a). Moreover, the characteristic asymmetric $\nu_{as}(NO_2)$ IR vibration frequency was shifted from 1552 cm^{-1} in the gas phase to 1526 cm^{-1} on TiO_2 and Au/TiO_2, indicating a strong interaction of the nitro group with the TiO_2 support. Detailed deconvolution of the $\nu_{as}(NO_2)$ IR band in the Au/TiO_2 sample shows the co-existence of a second component at lower frequency, i.e. 1520 cm^{-1}, related to a different molecular interaction, probably with metal-support interface sites (see Fig. 1b).

Simultaneously, the interaction of nitrostyrene with a series of catalyst models including single crystal Au(111) and Au(001) surfaces, a monoatomic row on a defective gold surface, an isolated Au_{38} nanoparticle, a small Au_{13} nanoparticle supported on TiO_2, and the TiO_2 surface, was theoretically investigated [7]. It is important to mention that all calculations in this and the other theoretical studies reported in this paper are based on periodic density functional theory (DFT) and were carried out using the Perdew-Wang exchange-correlation functional within the generalized gradient approximation (GGA) as implemented in the VASP code. Nitrostyrene was initially adsorbed on each catalyst model parallel and perpendicular to the catalyst surface, and in this last case with either the nitro or the C=C bond close to the metal atoms. It was found that nitrostyrene interacts weakly with extended Au(111) and Au(001) surfaces, with calculated adsorption energies lower than 3 kcal/mol and no significant changes in the molecular geometry, in agreement with the kinetic and IR data reported for Au/SiO_2. The interaction with low coordinated gold atoms present in the defective surface or in the Au_{38} nanoparticle is however non-negligible, and the optimized structures of the two adsorption complexes obtained over the Au_{38} nanoparticle model, depicted in Fig. 1d, show that the N—O (left) or the C=C bonds (centre) are activated by interaction with gold. However, the systems with the C=C bond directly interacting with gold are in all cases more stable than those with the nitro group attached to the metal, which would result in a low selectivity towards the aniline. Since these results don't match the experimental ones, the role of the support was then taken into consideration and nitrostyrene was adsorbed on the TiO_2 surface model. Due to the repulsion between the aromatic ring and the oxygen atoms of the catalyst surface, all attempts to locate a minimum corresponding to adsorption through the C=C bond evolved to the same structure (Fig. 1c) in which the molecule is perpendicular to the surface and the O atoms of the nitro group are directly attached to 5-fold coordinated Ti atoms. But the calculated interaction energy for this system is as large as −42 kcal/mol, suggesting that it might be too stable to participate in the reaction. Then, nitrostyrene was adsorbed at the metal-support interface and the other complex depicted in Fig. 1c was obtained. The O atoms