The non-innocent role of cerium oxide in heterogeneous catalysis: A theoretical perspective

M. Verónica Ganduglia-Pirovano*

Instituto de Catálisis y Petroleoquímica, Consejo Superior de Investigaciones Cientícas, Marie Curie 2, 28249 Madrid, Spain

A B S T R A C T

Ceria (CeO_2) is the most significant of the oxides of rare-earth elements in industrial catalysis with its reducibility being essential to its functionality in catalytic applications. The complexity of real (powder) catalysts hinders the fundamental understanding of how they work. Specifically, the role of ceria in the catalytic activity of ceria-based systems is still not fully understood. To elucidate it, well-defined ceria-based model catalysts are prepared experimentally or created theoretically and studied. The purpose of this brief review is to discuss recent results on model ceria-based catalysts using $CeO_2(1\,1\,1)$, $VO_x/CeO_2(1\,1\,1)$, and $Ni/CeO_2(1\,1\,1)$ as examples of catalysts for partial alkyne hydrogenation, oxidative dehydrogenation, and hydrogen production, respectively. The emphasis is here put on theoretical studies and special attention is given to the effects of ceria as catalyst support.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Ceria is a very popular component in catalytic applications such as the treatment of exhaust gases, where its ability to be reduced and reoxidized, and its oxygen mobility, play a crucial role [1,2]. In addition, ceria holds promise in a future hydrogen economy and associated fuel cell energy converters [3–6]. Typically, ceria is used as a catalyst carrier in combination with transition metals (e.g., Pd, Pt) and/or transition metal oxides (e.g., VO_x), magnifying the performance of the main active phase acting as a promoter, stabilizer, or cocatalyst; ceria alone has been so far of little interest as catalyst.

For oxide supported metal catalysts in particular, the term "strong metal-support interaction" has traditionally been used to describe the changes in the morphology of the metallic phase due to the presence of the oxidic support [7,8]. However, the support can also modify the electronic properties of an admetal [9–19] and the oxidation state of chemical species in supported metal oxide catalysts [20–23]. Moreover, the catalytic function of supported catalysts can be affected by a variety of factors, which include the already mentioned electronic structure changes in the adspecies through interactions with the support as well as adparticle size effects, the nanostructuring of the support itself, and changes in the reaction mechanism through the addition of new sites at the support that only play a synergistic role when near the supported

phase [24–28]. In many cases, metal ↔ ceria [29–31,12,10] and metal-oxide ↔ ceria [32,20,33] interactions have been proven to be crucial to achieving high catalytic performance. In practical terms, one wants to optimize the properties of both the adspecies and the oxide support and manipulate adspecies ↔ support interactions to improve catalytic activity and selectivity.

Real supported catalyst powders are very complex systems and a fundamental understanding of the above mentioned factors affecting catalytic activity is important for elucidating how these catalysts work. This understanding can be obtained by a reductionist approach consisting in creating and evaluating experimental and theoretical model catalysts that mimic the real catalysts in their complexity [34,35]. The feasibility of such an approach to date is undoubtedly due to recent advancements in characterization techniques and theoretical methods which have increased the general knowledge of complex systems. Certainly, the interplay between experiment and theory has been identified as essential to achieve deeper understanding. Admittedly, the greatest challenge in gaining knowledge that can ultimately aid in the rational design of better or new catalysts is to study the ever-more intricate model catalytic systems under relevant reaction conditions, and in so doing, bridge the often-discussed pressure and materials gaps between catalysis and surface science. In this regard, substantial progress has been made, but much more effort is needed.

In the following, we will discuss the non-innocent role of cerium oxide in heterogeneous catalysis, either as stand-alone catalysts or as a support, using the $CeO_2(1\,1\,1)$ surface as well as $VO_x/CeO_2(1\,1\,1)$ and $Ni/CeO_2(1\,1\,1)$ systems as examples of model

catalysts for partial alkyne hydrogenation, oxidative dehydrogenation, and hydrogen production, respectively. How important is the creation and study of theoretical and experimental model systems for understanding will be demonstrated. The emphasis is here put on theoretical studies, though knowledge of the real catalysts and results of experimental studies of model catalysts, as far as relevant for comparison, are briefly reviewed.

2. Models and methods

The use of the so-called periodic approach to model complex catalytic surfaces for heterogeneous catalysis in combination with plane-wave basis sets, is very common [36,37]. It consists of the simulation of an elementary cell, containing several tens to hundreds atoms and a vacuum layer, repeated periodically over three directions in space, defining a series of stacked slabs of solid material separated by empty spaces. The sufficiently thick vacuum layer avoids the interaction between surfaces of periodic images in the direction perpendicular to the surface. The complex active surface such as that of metal nanoparticles dispersed on transition metal oxides, and the presence reactants, are typically put on one side of the slab. Note that there are periodic approaches where localized atomic orbital basis sets are used and thus the elementary cell is repeated over two directions only. An alternative approach is the use of cluster models consisting of the simulation of a particle (representing the active phase) of a few to several tens of atoms [38] whereas the rest of the system is treated by so-called embedding techniques [39]. In the embedded cluster approach the refinement of the quantum treatment of the embedded local region to improve accuracy, is possible. Most theoretical studies of ceria-based systems employed periodic approaches, and the examples of embedded cluster models are rare [40,41]. Moreover, non-embedded cluster models of a sizable number of atoms can be used to simulate effects of surface nanostructuring, since they naturally provide a variety of different surface sites [42].

Density-functional theory (DFT) calculations have become a widely used tool for identifying local minima structures on the potential energy surface on which chemical transformations take place as well as for investigating the structures' atomic-scale properties. Moreover, DFT calculations can be combined with methods for locating transition states (saddle points) associated with catalytic processes [36,43]. One example of such methods is the nudged elastic band (NEB) method [44], where a set of replicas (images) of the system between the initial and final state is constructed, with a spring interaction between adjacent images. The optimization of the "band" of images, involving the minimization of the force acting on the images, brings the band to the minimum energy path. There are examples in which the complete kinetics of a catalytic reaction has been evaluated solely on the basis of DFT calculations of reaction barriers, reaction energies and the associated entropies [45,37]. However, the procedure for calculating all reaction energies and activation energy barriers for all possible elementary steps for a given system, is computationally very demanding, and becomes an impractical task when a large number of systems has to be screened. Rather, it is useful to identify which microscopic materials properties of the catalyst determine the macroscopic catalytic performance, i.e., to establish so-called reactivity descriptors [46].

The accuracy of DFT calculations depend on several choices among which that of the exchange-correlation functional plays a predominant role. Widely used approximations for the exchange-correlation functional are the local density or generalized gradient approximation (LDA and GGA, respectively). There are now many different flavors of GGA functionals available [47]; the PW91 [48] and PBE [49] functionals are most popular. In practice, the LDA yields very serious errors, strongly overbinding atoms into molecules and solids and onto surfaces. With regard to accuracy, GGAs reduces the overbinding, but still overbinds in most cases. A number of other failures are known to exist in LDA and all GGAs, for example the underestimation of band gaps, the gross overestimation of electron delocalization and metallic character, and the underestimation of energy barriers for molecular reactions. These shortcomings are a consequence of the approximations to the unknown exchange-correlation functional and the lack of exact cancellation of the Coulomb self-interaction energy, which stabilizes solutions with delocalization of the electron density. The delocalization problem is well-known when it comes to describing narrow-band electrons in transition-metal and rare-earth oxides such as reduced ceria [50,51]. The electrons gained by ceria upon reduction, occupy split-off states of the initially empty Ce $4f$ band, lying inside the O_{2p}–Ce_{5d} band gap of ceria and being highly localized in space. One way to minimize the self-interaction error is to mix a portion of non-local Fock exchange with the local LDA/GGA exchange-correlation potential. The functionals that do this are known as hybrid, and as with the GGAs, there is no unique way to construct a hybrid functional. Popular functionals are B3LYP [52], PBE0 [53–55], and most recently HSE [56,57].

A more pragmatic approach – and computationally more efficient than hybrid-DFT – to describe metal oxide systems containing localized d or f electrons, is the so-called DFT+U approach [58]. In practice, in these DFT(LDA/GGA)+U approaches one identifies a set of atomic-like orbitals that are treated with an orbital-dependent potential and associated effective screened on-site Coulomb interaction parameter, U [59]. In this method, at variance with the hybrid functionals, only a subset of correlated orbitals are considered whereas a large part of the exchange and correlation effects are still described with LDA/GGA, which suffers from the self-interaction error. Hence, questions regarding the proper way of specifying the atomic-like orbitals, and of deriving the best value for the U parameter are still under debate [60–62]. Nonetheless, most DFT+U studies of reduced ceria-based systems agree that U values for Ce $4f$ states in the range of 4.5–6.0 eV with GGA, are suitable. However, one should bear in mind that there is in general no unique U that gives a reasonable account of all systems' properties [63]. Moreover, one should also be aware of the existence of multiple self-consistent solutions in DFT+U [64], corresponding to different occupations of the m projections associated with the subshell l to which the U parameter is applied. Which solution a particular calculation reaches may depend on, for example, the U value, the initial orbital occupation, lattice geometry, and enforced symmetry.

A final important point to keep in mind is that DFT/DFT+U with LDA or GGAs as well as hybrid-DFT do not properly account for van der Waals (vdW) dispersive interactions, that are specially important for describing physisorption phenomena. In recent years, various approaches which account for vdW forces within the framework of DFT have been proposed (see Ref. [65] and references therein).

Theoretical studies for heterogeneous catalysis by ceria-based catalysts are challenging for DFT and without doubt, they represent a formidable task. As mentioned-above, the reduction of ceria implies narrow-band formation of $4f$ electrons and the concomitant presence of Ce^{3+} ions. Hence, the location of the reduced ions needs to be explored in order to find the global minimum of reduced ceria-based structures. This is a lesson that has been learned from DFT investigations of near-surface oxygen vacancies on CeO_2 surfaces that predicted the preference of the excess electrons for localizing on next-nearest neighbor Ce ions to the defects [66–68], in contrast to the generally accepted nearest neighbor cation sites. A subsequent study using scanning tunneling microscopy and spectroscopy in combination with DFT calculations has confirmed the theoretical predictions [69].