Catalysis Today 177 (2011) 1–2

Contents lists available at SciVerse ScienceDirect

Catalysis Today

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

Preface

The synergistic power of theory and experiment in the field of catalysis

This special issue of Catalysis Today is devoted to works combining experiment and theory. This type of research projects has become state of the art in various fields of exact sciences. In chemistry and physics this working procedure is now indispensable if one wants to understand processes occurring in the nanometer scale vicinity of surfaces or interfaces configuration [1,2]. The success of this setup is also translated in the number of special issues dedicated to it, and especially in the different fields related to catalysis: heterogeneous and homogeneous catalysis, electrocatalysis, surface science, gas-phase cluster reactivity, etc., see for instance Refs. [3,4].

Recent experimental science, when applied to analyze nanometric scale phenomena, rely more and more on theory, so that the acquired data are necessarily interpreted with numbers and models. A good model not only helps experimentalists to rationalize their results, but also help make predictions that challenges the capability of available experimental techniques in terms of the spatial, time and energy resolutions, and guide experimentalists to design new experiments [2]. The role of the contemporary theoreticians is beyond deriving theories and methods accurate enough to characterize and predict the physicochemical properties of matter. It is moreover developing models to interpret the experiment, but with cleverness because as Einstein once said, a model should be as simple as possible but not simpler.

Following the present day developments in science and technology one can imagine that in the (near) future theory and experiment merge together. This convergence is strongly supported with the evolution of technology and computer power in particular, illustrated by the famous law of Moore. Consequently experiments evolve to computational experiments, and theoretical calculations evolve to applied computational chemistry, which can also be considered as computational experiments.

Prof. Avelino Corma, a world-known catalytic chemist, kindly accepted to give us his view, as an experimentalist, on combing theory with experiment. To our question, what does an experimentalist expect from theory, he answers: “There are different aspects of catalysis that cannot be directly measured today by experimental techniques and benefit from the information provided by theory. One of them is the possibility of proving or refusing starting hypothesis on the basis of theoretical calculations, thus directing the design of the experiments and reducing the number of variables that have to be considered or explored. Theory is also a fundamental tool to establish general rules of behavior, and this applies to catalysts, to reactants, and to the way of interaction between them. Finally, an experimental catalytic chemist always expects from theory help in the interpretation at a molecular level of results provided by experiments”.

The way of facing research in catalysis has considerably evolved. Catalysis was born as an empirical applied field where the reactivity tests played the central role in the process. Based basically on trial-error approach, the development of a catalyst benefits now from a pluridisciplinary point of view where computer simulations join the traditional synthesis and characterization steps. The computational research improvements, both on the computer power and the implementation of robust and efficient algorithms, together with the visualization tools, made calculations accessible to the catalytic community. These developments made accessible the *per se* difficult task of modeling a real complex material. Let us take the example of zeolites to illustrate the evolution in the modeling process. Zeolites are well known systems in the field of catalysis. Zeolites started being studied very early using theory and computational chemistry. The first non-empirical calculations were performed on models containing a few atoms as early as 1972–1973 [5,6], namely the famous $Si(OH)_4$ molecule and the disiloxane bridge containing an Al atom. These models of less than 10 atoms were used at the end of the 70s by pioneer researchers such as Mortier et al. [7,8] and Sauer et al. [9,10] among others. In the late 80s and 90s the first ring structures and other primary zeolite building blocks appeared using *ab initio* methods, as can be seen e.g. in the early works of Goursot et al. [11–13]. During the 90s the clusters of zeolites calculated using quantum chemical codes contained up to 50–100 atoms [14]. The success in the implementation of periodic boundary conditions in user-friendly codes allowed in the last years to model large cages of zeolites otherwise unaffordable like e.g. Mordenite [15], BEA [16,17], etc.

Indeed, the development of efficient codes and parallel computing has showed its reliability in the treatment of a wide variety of physico-chemical phenomena [18–21]. This milestone changed theoretical material science drastically, and has still a strong impact today. As can be seen in the collection of papers presented in this special issue, more and more realistic models are proposed, calculated, and successfully interpreted in synergy with experiment.

In this special issue the systems covered include both concepts and application in the fields of heterogeneous catalysis, surface science, gas-phase clusters, electrocatalysis or organometallic chemistry, illustrating the power of the multidisciplinary approach. The first part considers metal oxides in a variety of catalytic presentations: supported, zeolites or modified by the addition of metals, aiming at elucidate structure-reactivity relationships. A second part is devoted to the characterization of metallic surfaces by

0920-5861/$ – see front matter
doi:10.1016/j.cattod.2011.08.026

surface science techniques and density functional theory (DFT); it brings important information on the crucial role of surface species. Finally, a series of three papers shows how gas-phase clusters and organometallics chemistry provide a rich playground for the comprehension of catalytic processes from the fundamental point of view. Let us briefly present each of the valuable contributions to this special issue. All of them have been carefully selected to focus on the use of theory to gain understanding on specific experimental findings, and most of them present both experimental and theoretical results together.

The first paper is devoted to the comprehension of the support effect in supported vanadium oxides. The support is known to a play key role in catalytic redox processes, its effect on the molecular level is still not well understood. Frank De Proft and co-workers do a step forward in this direction using reactivity concepts to quantify the vanadium-oxygen bond for a series of catalytic oxide supports.

Karen Hemelsoet and co-workers have investigated the methanol and ethanol conversion over an acidic H-SAPO-34 catalyst. A new theoretical procedure based on a normal mode analysis allows the interpretation of the experimental IR spectra and gives insight in the key role of framework–guest interactions.

The location and environment of transition metals strongly determines the reactivity in metals-exchanged zeolites. Pascale Massiani and Hazar Guesmi show that the coordination and local environment of Ni^{2+} cations in dehydrated Ni/NaX faujasites can be determined precisely by combining experimental (X-ray absorption spectroscopy, XAS) and theoretical (DFT) techniques.

Gloria Preda and Gianfranco Pacchioni use first principles calculations to investigate the soot combustion in particulate Diesel filters by means of ceria modified catalysts. The addition of silver atoms on CeO_2 surfaces together with the presence of oxygen vacancy defects, induce the formation of surface species able to determine the catalytic reactivity.

The impact of self-assembling on a polar surface is studied by Dominique Costa and her team. It is concluded that carboxylic acids adsorb dissociatively on the Zn–ZnO(0 0 0 1) surface. Dispersion forces are found to be responsible for interchain interactions leading to a tilted configuration. The formation of an organic monolayer over an oxide surface provides coating properties with implication for instance in corrosion processes.

Metallic surfaces are ideal systems to apply surface science techniques as well as DFT. Thus, XingQiang Shi and co-workers investigated the thermally activated transformation of the adsorption configurations of a complex molecule on a Cu(1 1 1) surface. It is demonstrated that the combination of scanning tunneling microscopy (STM) measurements and DFT calculations is very efficient in probing the atomic details of molecular adsorption configurations on surfaces.

Elizabeth Santos and co-workers investigate the unique properties of submonolayer Pd–Au nanostructures in hydrogen oxidation/evolution electrocatalytic reactions. The combination of STM and DFT brings valuable information on the structure of such nanoparticles. The application of the electrocatalysis theory allows explaining quantitatively the results found.

Gas-phase cluster experiments have proven to be a powerful tool in the comprehension of reaction mechanisms in a variety of fields. Elliot Bernstein and coworkers succeeded to generate neutral gold carbonyl clusters. These clusters are characterized as regards their reactivity towards N_2O and O_2. Explicit consideration of relativistic functional considerably improves the theoretical description of the reaction mechanisms taking place.

The group of Rosa Llusar investigated the catalytic gas-phase acetaldehyde formation by tungsten (IV) complexes. The results, obtained by the combination of collision induced dissociation experiments and DFT, point to a competition between two mechanisms for the key step in the reaction, the hydrogen transfer.

The reactive properties of copper–oxygen adducts is studied by Hélène Gerard and coworkers. DFT calculations performed for a series of ligands allow proposing a reaction mechanism for the stabilization of the dioxygen molecule on the metallic center, a crucial stage in many enzymatic and biological catalytic reactions.

Finally, we would like to thank all the authors for their enthusiastic response and their effort to submit high-quality contributions in a rich variety of topics. We also want to thank the editorial and production staff for their assistance, and especially M. Bañares who encouraged us to go on with this project. A. Corma is also acknowledged for his support and constructive discussions. We hope that this special issue will provide a valuable reference and perspective of the state-of-the-art in investigating catalytic systems.

References

[1] G.A. Somorjai, Introduction to Surface Chemistry and Catalysis, Wiley, New York, 1994.
[2] G.A. Somorjai, Y.M. Li, Top. Catal. 53 (2010) 311.
[3] H. Metiu, J. Chem. Phys. 128 (2008) 182501.
[4] A. Markovits, M. Calatayud, C. Minot, J. Mol. Struct. (THEOCHEM) 903 (2009) 1.
[5] G.A.D. Collins, D.W.J. Cruickshank, A. Breeze, J. Chem. Soc. Faraday Trans. 2 (1972) 1189.
[6] T.L. Gilbert, W.J. Stevens, H. Schrenk, M. Yoshimine, P.S. Bagus, Phys. Rev. E: Solid State B8 (1973) 5977.
[7] W.J. Mortier, S.K. Ghosh, S. Shankar, J. Am. Chem. Soc. 108 (1986) 4315.
[8] W.J. Mortier, K. Vangenechten, J. Gasteiger, J. Am. Chem. Soc. 107 (1985) 829.
[9] J. Sauer, P. Hobza, R. Zahradnik, J. Phys. Chem. 84 (1980) 3318.
[10] J. Sauer, Chem. Rev. 89 (1989) 199.
[11] A. Goursot, F. Fajula, C. Daul, J. Weber, J. Phys. Chem. 92 (1988) 4456.
[12] L. Campana, A. Selloni, J. Weber, A. Pasquarello, I. Papai, A. Goursot, Chem. Phys. Lett. 226 (1994) 245.
[13] I. Papai, A. Goursot, F. Fajula, J. Phys. Chem. 98 (1994) 4654.
[14] F. Tielens, W. Langenaeker, A.R. Ocakoglu, P. Geerlings, J. Comp. Chem. 21 (2000) 909.
[15] T. Demuth, J. Hafner, L. Benco, H. Toulhoat, J. Phys. Chem. B 104 (2000) 4593.
[16] B.S. Kulkarni, S. Krishnamurty, S. Pal, Chem. Phys. Lett. 484 (2010) 374.
[17] A. Wojtaszek, M. Ziolek, S. Dzwigaj, F. Tielens, Chem. Phys. Lett. (2011), doi:10.1016/j.cplett.2011.08.005.
[18] M.M. Islam, D. Costa, M. Calatayud, F. Tielens, J. Phys. Chem. C 113 (2009) 10740.
[19] F. Tielens, M. Calatayud, A. Beltrán, C. Minot, J. Andrés, Electroanal. J. Chem. 581 (2005) 216.
[20] T.V. de Bocarmé, T.-D. Chau, F. Tielens, J. Andrés, P. Gaspard, L.R.C. Wang, H.J. Kreuzer, N. Kruse, J. Chem. Phys. 125 (2006) 054703.
[21] F. Tielens, J. Andrés, J. Phys. Chem. C 111 (2007) 10342.

Frederik Tielens [a,b]
[a] *UPMC Univ Paris 06, UMR 7197,*
Laboratoire de Réactivité de Surface,
F-75005 Paris, France
[b] *CNRS, UMR 7609,*
Laboratoire de Réactivité de Surface,
F-75005 Paris, France

Monica Calatayud [a,b,*]
[a] *UPMC Univ Paris 06, UMR 7616,*
Laboratoire de Chimie Théorique,
F-75005 Paris, France
[b] *CNRS, UMR 7616,*
Laboratoire de Chimie Théorique,
F-75005 Paris, France

[*] Corresponding author at: CNRS, UMR 7616,
Laboratoire de Chimie Théorique,
F-75005 Paris, France.
*E-mail address:*monica.calatayud@upmc.fr
(M. Calatayud)