

Application of computational methods to catalytic systems

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Abstract

An analysis of the complexity involved in the computational modeling of catalytic reactions is presented, including a review of applications and limitations of ab initio methods in this context. The foundations of parametric methods based on simulation techniques and the use of elementary parametric energy functionals are briefly discussed. We describe the implementation and facilities of a quantum-chemical package, usually referred to as CATIVIC, especially tailored for catalytic processes. Finally, the application of this code to catalytic systems is illustrated with several examples.

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1. Introduction

The importance of catalysis may be exemplified by the following facts: (i) the synthesis of about 60–80% of industrial chemicals relies on catalysts [1,2]; (ii) the world market for catalytic products is about US\$ 10 trillion [3]; and (iii) the total investment on royalties and licenses in the field is more than US\$ 3 billions [4]. In addition, catalysts are being massively used in automobile emission control and, more recently, in very selective devices in indoor environments [5,6] for the elimination of tobacco smoke and nasty toilet odors and in garbage disposal. Also for volatile organic compounds (VOCs) in cooking, wood products, plastics, office equipment, glues, the treatment of microbial contamination from ventilation systems and domestic water pollutants. In general, the quality of life is to improve by using “smart catalytic” devices – catalysts that modify their activity depending on a

coupled sensor – or “intelligent materials”. Catalysts are also useful in the synthesis of chiral pharmaceutical compounds and in cleaning water, air and soil pollution.

A new generation of highly selective catalysts will be obtained from the synthesis of nanoparticles supported on surfaces, encouraging most of the major chemical and petrochemical corporations to invest significant resources on nanocluster research. Furthermore, applications of cluster chemistry are relevant in different technological disciplines: the recording industry, in metallurgic and high-electronic technology, miniature magnets, quantum-dot lasers, single-electron transistors, thin films, Josephson devices, semiconductor memory, optical storage, colloids, coating, seals, encapsulants, sensors, electro-optical microelectronics, xerography, biomedical devices and batteries.

The catalytic properties of clusters are somewhat different from those in extended solids [7–9]. Despite of the great developments of modern quantum-chemistry (QC), many approximations have to be made in the modeling of industrial catalysts in order to obtain results in tractable computational

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times. Somorjai and coworkers [10] suggest that “Model catalysts could be and should be designed to possess all the complexity of multicomponent of sophisticated industrial catalysts without the high surface area.” The application of cluster models to understand the phenomena of chemisorption and catalysis is not new, they have been around for decades [11]. In fact, clusters are not only useful as surface models but can be synthesized as fundamental components of catalysts and electronic devices [12–15]. However, there are practical problems in carrying out accurate calculations for intermediate cluster sizes using *ab initio* methods. The computation of accurate electronic properties requires electron correlation energies and, for very heavy atoms, the inclusion of relativistic effects. Therefore, there must be a tradeoff between model size and accuracy. Atomic geometrical arrangements are critical to cluster properties, and the adsorption energy usually oscillates with cluster-model size [16]. The difficulty in finding global minima [17] is that optimization with classical potentials [18] is still widely used instead of a direct QC geometrical energy minimization. Moreover, clusters are dispersed on solid supports that, in many cases, have a strong effect on reactivity properties. Reaction mechanisms in surface catalysts are very complex and normally require reactive ensembles (sets of active sites involved in a particular reaction step) and reactive aggregates (collections of reactive ensembles necessary for the formation of a product).

The importance of this topic is supported by the recent huge effort made in the European Union with the QUANTUM Simulation in Industry (QUASI) project [19]. In this project different well-known quantum-chemistry (GAMESS-UK, TURBOMOLE, MNDO, VASP) and classical (CHARMM, GULP, AMBER, DL_POLY, GROMOS) codes, among others, have been integrated in a quantum mechanics/molecular mechanics (QM/MM) scheme. It is significant that the first tasks to be tackled correspond to the modeling of Cu/ZnO, Cu/zeolite and enzymes catalysts.

In this work we analyze the complexity of: catalytic processes in different areas of chemistry, physics, and engineering; quantum catalytic modeling; surface processes; and energy flux at the reaction center. A survey of the most recent and relevant computational modeling work using *ab initio* methods is also carried out in Section 3. In Section 4, the alternative of using quantum-chemistry parametric methods is presented. Several examples have been selected in Section 5 relating zeolite catalysts and the formation of biological molecules on graphite platelets. Finally, some comments and remarks are given in Section 6.

2. Complexity of catalytic processes

The life of an industrial catalyst involves a succession of steps: preparation → activation → operation → deactivation → regeneration. However, most of the theoretical modeling is concerned with the reactions involving the catalyst during the catalytic process. Others processes are not modeled

because of their complexity, in particular, catalyst preparation. The latter is of vital importance because it allows the generation of the desired and adequate active phase, particle size, surface structure, composition, and oxidation states for particular selective catalyst properties. It is the know-how of industrial efficient catalysts.

Catalysis research involves interdisciplinary areas of science and engineering, in the same way that catalytic modeling entails several disciplines: quantum-chemistry, classical mechanics, molecular dynamics, Monte Carlo, kinetics, fluid dynamics, thermodynamics and process engineering. A simple scheme for the complete modeling of the whole catalytic process and the connection between different branches of research are displayed in Fig. 1. Quantum-chemistry is the source of information to be coupled with other areas of science in order to obtain macroscopic properties. The gap between the microscopic information obtained from QC can be extended to realistic systems using statistical techniques and classical potentials. Quantum molecular dynamics employing Car-Parrinello schemes are shown as dotted lines from QC to thermodynamic properties and reaction velocity constants. Theoretical results can be integrated into microkinetic models by using Monte Carlo methods, velocity and diffusion constants to obtain product distribution, reaction mechanism and possible intermediates. It may be noted that the whole range of phenomena to be modeled range from Angstroms to meters and from femtoseconds to hours.

Practical QC calculations, as mentioned above, are a compromise between the theoretical framework and the size of the selected model. Modeling catalytic reactions comprise several stages (see Fig. 2). (a) Location of reactive adsorption sites and adsorption modes for a molecule on a selected surface. This is normally done by trial and error, starting at different adsorption site locations with various adsorbate orientations. Bader's theory of reactivity (topology of the density Laplacian) is perhaps a powerful tool to establish the location and properties of adsorption sites, as well as the optimal orientation of an adsorbate on the surface [20,21]. (b) Adsorption requires the evaluation of potential energy curves (PECs) that provide information on bonding, orbital interaction, and electronic charge transfer change during the process. The existence of a precursor state (physisorbed molecule) may appear before chemisorption occurs. It is convenient, but very expensive, to carry out optimizations of both the adsorbate and substrate in each PEC step at fixed adsorbate–surface distances in order to analyze relaxations throughout the adsorption process. (c) Adsorption may occur by excited molecules, excited adsorption sites or both of them. For example, Nienhaus [22] concluded that electronic excitations are phenomena that occur in exothermic reactions on metallic surfaces. The importance of surface and adsorbate excited states has not as yet been considered in standard QC modeling of catalytic reactions. (e) Adsorption leads to surface reconstruction as a result of significant relaxations due to surface–adsorbate bond formation. This issue has been well established in surface science physics [23,24]. (f) Bond activation is a relevant

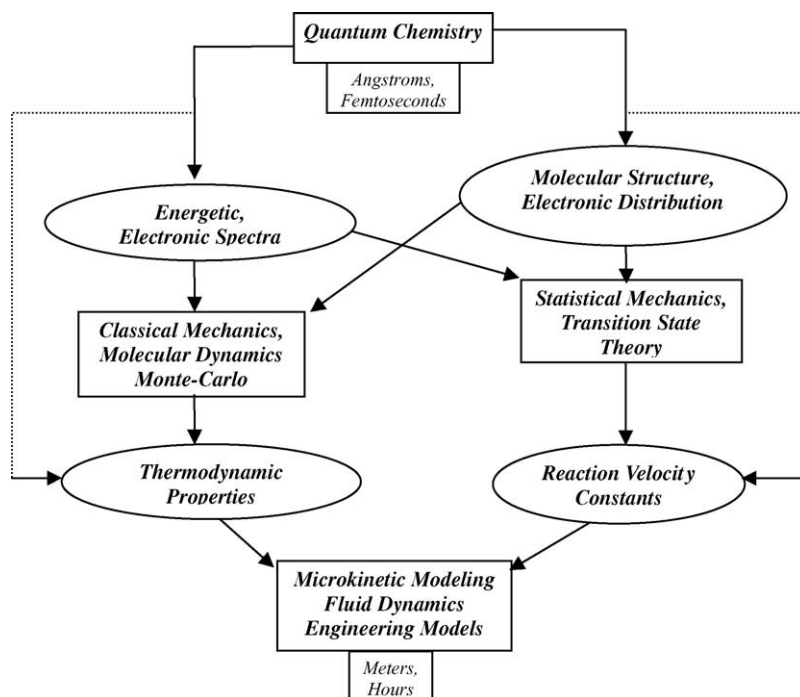


Fig. 1. Different theoretical disciplines needed in the modeling of catalytic reactions from micro to macro properties.

issue that leads to bond breaking and the generation of new compounds. It is useful to have the facility for evaluating bond strength in the computational package. (g) As pointed out by Haber [25], "The phenomenon of catalysis may be explained in terms of the nature of intermediate complexes formed on interaction of the reacting molecule with the group of atoms of the catalyst." Many intermediate complexes may occur in a catalytic process as shown by Zaera [26] in the surface chemistry of hydrocarbon fragments. (h)

The Langmuir–Hinshelwood model [27] of surface reactions implies the diffusion of reactants on the surface; therefore, potential energy barriers along several directions must be evaluated. (i) Previous dissociations of adsorbed species may take place before the surface reaction occurs [28]. (j) The knowledge of reaction pathways and activation barriers for surface reactions is fundamental for improving catalyst selectivity [29]. (k) Surface desorption is a relevant process because catalyst life-span depends on product residence time [30]. This

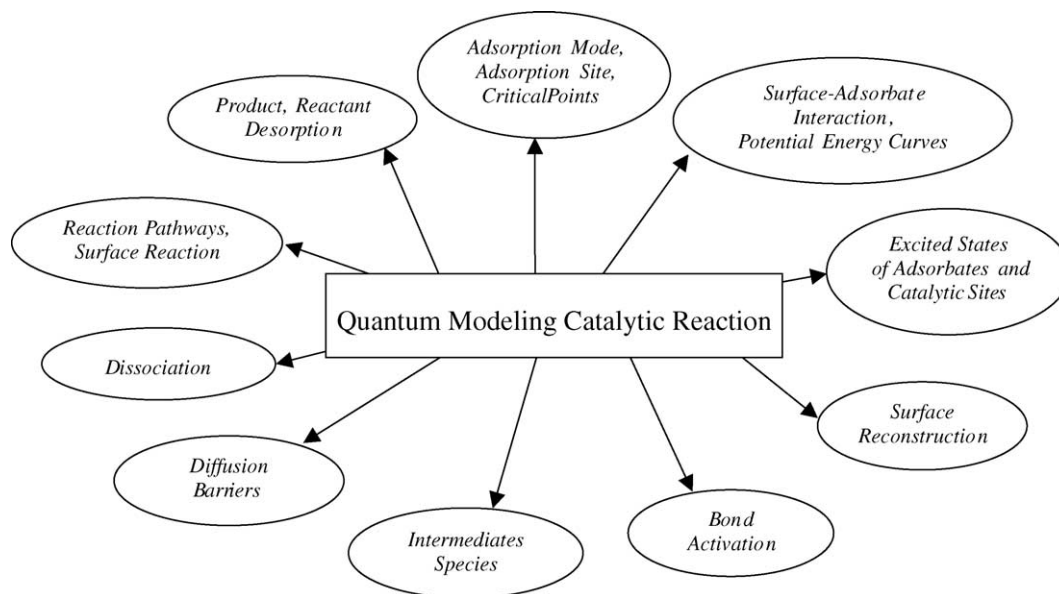


Fig. 2. Processes to be considered in the quantum modeling of a catalytic surface reaction.

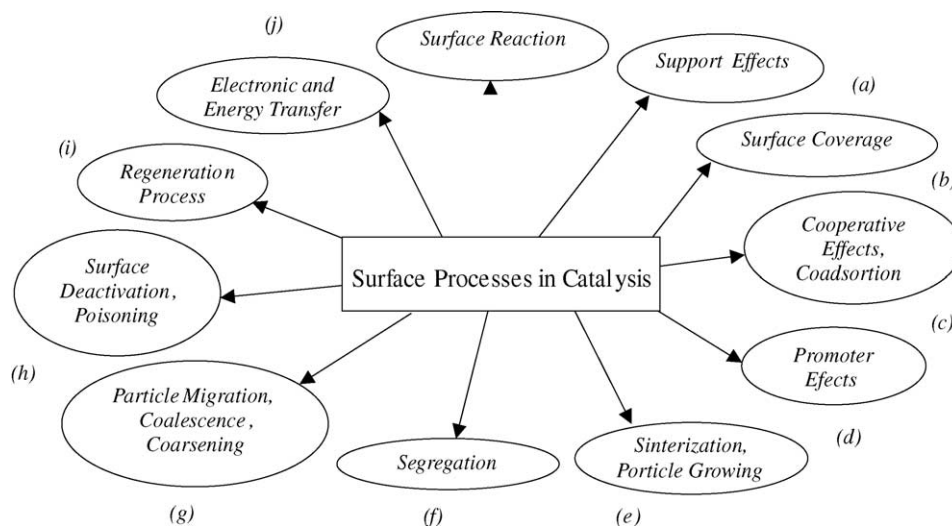


Fig. 3. Surface processes occurring in catalytic reactions.

is also important for modeling thermally programmed desorption (TPD) techniques that are useful in surface chemistry [10].

In addition to surface reactions, several other processes are simultaneously taking place relating a surface catalyst. A schematic scenario is presented in Fig. 3. (a) It is well known that the support has important effects other than leading to a more effective dispersion, but support–cluster bond interaction affects the adsorption site reactivity [10,31]. (b) Many catalytic reactions rely on surface coverage (island formation). Surface chemical reactivity in general effectively depends on surface adsorbate concentration [32]. (c) Coadsorption and cooperative effects, even for weakly adsorbed molecules, are very important as proposed by Iwasawa [33]. Coadsorbed molecules are able to assist and activate the reaction of strongly adsorbed intermediates that control the catalytic reaction path. (d) Addition of promoters is a standard way to improve the activity of catalysts [34]. (e) The growth of adsorbed clusters on a support is a common phenomenon that takes place on catalytic surfaces [10,35]. (f) Migration from the bulk to the surface (segregation) may occur changing the catalytic surface composition [36]. (g) Particle diffusion, coalescence, and coarsening are very important processes of relevance in the synthesis of supported metal crystallites [37]. (h) Catalysts are deactivated by the poisoning of active sites or by the formation of graphitic carbon deposits [38]. (i) Active site regeneration and processes are very important for practical and economical reasons in industrial catalysts. (j) Finally, the understanding of electronic and energy transfer from the reactive ensemble to the neighboring atoms (support) is also a main issue as will be shown below.

According to Borowiak's model [30], a catalyst possesses five components: energy source, catalytic center, reactant, product molecule (PM), and energy dissipater. A simplified model of energy transfer in an elementary catalytic system is shown in Fig. 4. Four cases may be considered. (i) PM leaves

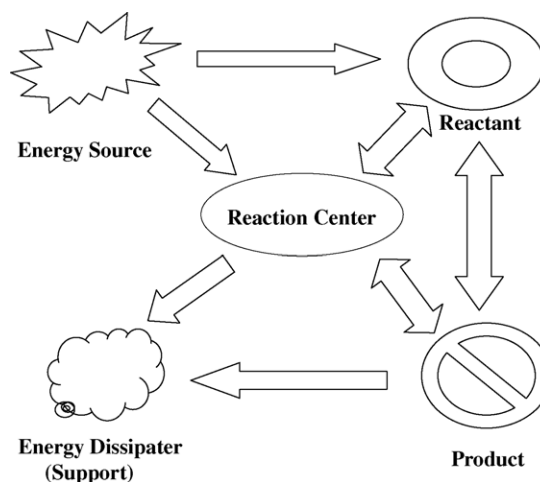


Fig. 4. Energy flux in a reaction center.

the active site if it has an energy greater than the heat of desorption because it has not been immediately dissipated. (ii) The active site is blocked if the time for energy dissipation is shorter than that for other molecular processes. (iii) The inverse reaction can occur if energy dissipation time is too slow especially for exothermic reactions. (iv) Consecutive and secondary reactions may happen if energy dissipation is lengthy. Note that this model may be applied to Eley–Rideal as well as Langmuir–Hinshelwood reaction mechanisms.

3. Ab initio methods in catalysis

The application of ab initio quantum calculations (ABQC) to catalysis has continuously grown in recent years. For example, in journals such as the *Journal of Catalysis* which traditionally is exclusively dedicated to experimental catalysis,

publication of ABQC have consistently increased in the last 4 years: 6, 7, 11, and 27 articles with DFT calculations published in 2000, 2001, 2002, and 2003, respectively. Moreover, during the same period the *Journal of Molecular Catalysis A* published 74 articles on this topic. *Catalysis Today* published an especial issue (#3–4) in 1999 dedicated to the progress of quantum-chemistry in catalysis entitled “*Advances and applications of theory and simulation to heterogeneous catalysis*”. The expansion of ABQC in the field of catalysis is mostly due to advances in computing capabilities (larger memories, faster and cheaper CPUs). The times of expensive big mainframes have been left behind.

As mentioned above, ABQC in catalysis have increased significantly in the last few years. For practical reasons, we present here a short outline of recent reviews, some relevant contributions, and the shortcomings of ab initio methods in this area. Several reviews have been published in the last three years such as “*The virtual chemistry laboratory for reactions at surfaces: Is it possible? Will it be useful?*” by Groß [39]; “*Perspectives on the first principles elucidation and the design of active sites*” by Neurock [40]; “*Applications of molecular modeling in heterogeneous catalysis research*” by Broadbelt and Snurr [41]. It is also important to consider reviews to other related areas of catalytic synthesis such as “*The impact of theoretical methods on solid-state chemistry*” by Dronskowski [42], and “*Computations and the future of materials physics*” by Rice [43].

In addition to the topics previously reviewed, we present some interesting applications of ABQC that show theory–experiment accord. Yajima et al. [44] reported an original application of computer-aided design of a novel catalyst using a combinatorial computational chemistry approach. Results predict that Ir^{3+} and Ti^{3+} ion-exchanged ZSM-5 catalysts, among three other metals (Cu^+ , Fe^{2+} , Co^{2+}), are the best deNO_x catalyst because of their high resistance to SO_x poisoning. Rodríguez [45] has extensively studied orbital-band interactions and the reactivity of molecules on oxide surfaces to explain trends in the interaction of many adsorbates with oxide surfaces. A clever connection of DFT calculations with industrial reactor design and catalyst selection for ammonia synthesis has been performed by Nørskov and coworkers [46]. Aray et al. [47], using electron density topology of pyrite-type transition metal sulfides, explained the experimentally observed reactivity volcano curves. An improvement of the description of Pd(1 1 1) adhesion to $\alpha\text{-Al}_2\text{O}_3(0 0 1)$ has been carried out by Mattsson and Jennison [48] that computed accurate surface energies and showed the importance of electron self-energy in metal/metal-oxide adhesion. On the other hand, Sautet and coworkers [49] made an very good theoretical and experimental correlations in strained structure of a four-layer deposit of Pd on Ni(1 0 0).

In order to have one idea of the possibilities of ABQC regarding model size, we present some significant examples. Analyzing the H adsorption at the Cu(0 0 1) surface using a periodic super-cell approach or employing finite clusters, Illas and coworkers [50] found that the convergence in bind-

ing energy and bond distances in the fourfold site is not achieved even for clusters of ~ 100 atoms. The cluster model approach is incapable of reproducing accurately the charge density and electrostatic potential of extended surfaces in Cu clusters.

Hydrodesulfurization (HDS), the removal of sulfur-containing molecules from heavy oil, has received much attention in the field of quantum-chemistry calculations. The VASP program [51] and a large super-cell ($9.48 \text{ \AA} \times 20.0 \text{ \AA} \times 12.294 \text{ \AA}$) was used by Payen and coworkers [52–54] to model the (1 0 0) Mo-edge and S-edge of MoS_2 surfaces in order to investigate the $\text{H}_2\text{-MoS}_2$ interaction from the thermodynamic point of view [53,54], evaluating the changes in the chemical potentials and the Gibbs free energy. Their main conclusion is that the formation of vacancies on the edges of the MoS_2 is an unfavorable process from the thermodynamic point of view. Similar results have been reported for CoMoS and NiMoS systems [55] using also the VASP package.

Delmon and coworkers [56], using a Pentium II computer with the GAMESS-US package [57], performed Hartree-Fock calculations on Mo_7S_{24} , Mo_7S_{12} , and Mo_7S_9 clusters in order to study the activation processes by H_2 . It was found that the reaction of H_2 with MoS_2 clusters was endothermic. Analyzing a bigger cluster, $\text{Mo}_{27}\text{S}_{54}$ [58], the authors concluded that there are two types of twofold unsaturated sites (CUS): those on the corners are potentially active sites for HDS reactions while the others on the (10 $\bar{1}$ 0) edges are only reactive to π -bond activation.

Orita et al. [59] optimized the $\text{Mo}_{27}\text{S}_{54}$ cluster in order to mimic the MoS_2 catalyst, employing a numerical double-zeta basis set, ECP for Mo atoms, and the generalized gradient corrected (GGA) DFT approach. Theoretical results agree well with the EXAFS data of dispersed unsupported MoS_2 . The authors found [60] from full geometry optimization and vibrational analysis that the adsorbed thiophene on a $\text{Mo}_{16}\text{S}_{32}$ cluster has the most stable configuration in a flat adsorption parallel to the (30 $\bar{3}$ 0) plain.

On the other hand, Raybaud et al. [61,62], using the ab initio VASP program [51] with a unit cell of 72-atoms ($\text{Mo}_{24}\text{S}_{48}$) studied the reorganization of the MoS_2 surface due to the vacancy formation processes [61], as well as the electronic properties of MoS_2 promoted surface by Co, Ni and Cu [62] (CoMoS, NiMoS, and CuMoS). The authors concluded that the most favorable promoter (Co or Ni) localization is the substitution of Mo atoms by Co or Ni located at the edges of the catalyst. In addition, sulfur-metal bond strengths follow the trend: $\text{MoS}_2 > \text{Co}_{0.33}\text{Mo}_{0.67}\text{S}_2 > \text{Co}_{0.67}\text{Mo}_{0.33}\text{S}_2 > \text{Co}_1\text{Mo}_0\text{S}_2 > \text{Ni}_1\text{Mo}_0\text{S}_2 > \text{Cu}_1\text{Mo}_0\text{S}_2$.

Hybrid computational schemes have been applied to the zeolite field. Atoguchi and Yao [63], using ONIOM method [64] and a cluster model of a MFI zeolite containing 200 atoms, made an investigation on Ti sitting in a MFI framework. The results suggested that the T9 and T10 are thermodynamically the more stable sites. Milas and Nascimento

studied the interaction of isobutane with zeolites using DFT-B3LYP on a 5T [65] and a double-ring 20T clusters [66]. The results show that the activation energy decreases with increasing cluster size.

Czekaj et al. [67–69] have analyzed the $V_2O_3(0001)$ surface by means of DFT with cluster models of different sizes. They found that large clusters, used to mimic different surface terminations, yielded similar electronic results for bulk vanadium and oxygen centers thus demonstrating the validity of the cluster approach for V_2O_3 systems [69]. On the other hand, the oxygen layer termination exhibits stronger relaxation of sub-surface vanadium layers than other layers which results in an increase in the ionic charge at the surface [68]. Bonding in V_2O_3 can be described by a mixture of ionic and covalent contributions, and the base/acidic properties of oxygen/vanadium sites scale with their coordination number [69].

Dynamics of clusters (Pd_{64}) adsorbed on a support ($Al_{384}O_{576}$) have been performed by Cruz Hernández and Fernández Sanz [70]. A combination of classical pair potentials (metal–metal and metal–surface) obtained from DFT and classical molecular dynamics simulation was carried out with the DL.POLY code [71]. Results reproduce the experimental findings that at a temperature of 500 K the Pd atoms diffuse into the alumina bulk.

Notwithstanding the large number of successful ABQC in modeling catalytic steps, there are some drawbacks [39] that must be mentioned.

- (a) High level ABQC remain prohibitively expensive for large amorphous systems.
- (b) Bonding cannot be described by a single determinant (DFT) for open-shell molecules on surface TM oxides with a localized d shell [72,73].
- (c) Super-cells are not large enough to model “real” nanostructures.
- (d) DFT is not well suited to address electronically excited states. It requires the use of time-dependent DFT for quantum dynamics [74].
- (e) Relativistic effects for heavy TM, actinides and lanthanides have to be considered.
- (f) Band gaps are unsatisfactorily underestimated by DFT.

As we can see in this short review, ABQC have progressed enormously; however, for practical purposes there are still many challenges to be overcome. The future of ABQC is promising taking into account the outstanding yearly growth of computer performance. Nevertheless, the number of steps to be modeled in catalytic processes is vast and with many reaction intermediates, non-uniform surface structures, and multiple reaction paths; in other words, there is a high complexity. Considering that nanoparticles appear as fundamental components in the new stereoselective catalysts, then more details and accuracy are required from theoretical modeling in order to satisfy technological requirements.

4. Parametric methods

Quantum-chemistry methods are normally based on the evaluation of the wave function (Hartree-Fock [HF], configuration interaction [CI], many-body perturbation theory [MBPT], coupled cluster [CC], etc.) or the density functional (DFT). However, all of these methods, as mentioned above, are very inefficient for massive calculations of multiple processes in large complex systems, such as the catalytic structures shown in Section 2. There is an avenue that still has a lot of unexplored possibilities: the quantum parametric approach or semiempirical methods. In these methods, the wave function is not derived, and the integrals or elementary functionals of the Hamiltonian operator are expressed in terms of interacting parametric functionals. These functionals are properly designed to simulate components of atomic and electronic interactions so as to reproduce several experimental or well-calculated properties of a set of molecular systems. Advantages and drawbacks of those methods are described as follows.

- (a) Integral calculations are not time consuming because most of them are evaluated from parametric functionals; therefore, these methods are faster than the rest of the QC methods.
- (b) The fundamental bases of parametric methods are well understood in terms of simulation techniques [75,76], which are used to define the set of parametric functionals. A precise representation of the Hamiltonian can be selected as reference for simulations; for example, a configuration interaction (CI) energy functional. Simulation of energy functional components is fundamentally substantiated by means of the generalized Weierstrass's theorem. The virial and Hellmann–Feynmann theorems may be incorporated as parameterization constrains [77]. Minimax and variational principles can be established in terms of corrected simulated functionals [77,78].
- (c) The main drawback is the troublesome parameterization process and a correct selection of parametric functionals to ensure accuracy. Parameters and functionals are obtained in a way not normally included in parametric codes. Therefore, programs for optimization of parameters and functionals are not available to users, as it occurs with standard ab initio methods where the optimizations of the basis set and active space and configuration selection are customary tasks.
- (d) The use of a minimum basis set can be addressed by the concept of Optimized Transformed Minimum Basis Set (OTMBS) [77]. It is explained by considering different auxiliary basis sets for dissimilar local environments in which electronic interactions are represented. Several orthogonality conditions related to these basis sets have been established.
- (e) The accuracy of these methods depends on the selection of the parametric functionals. Parametric and ab initio methods may be complementary. Small molecules can

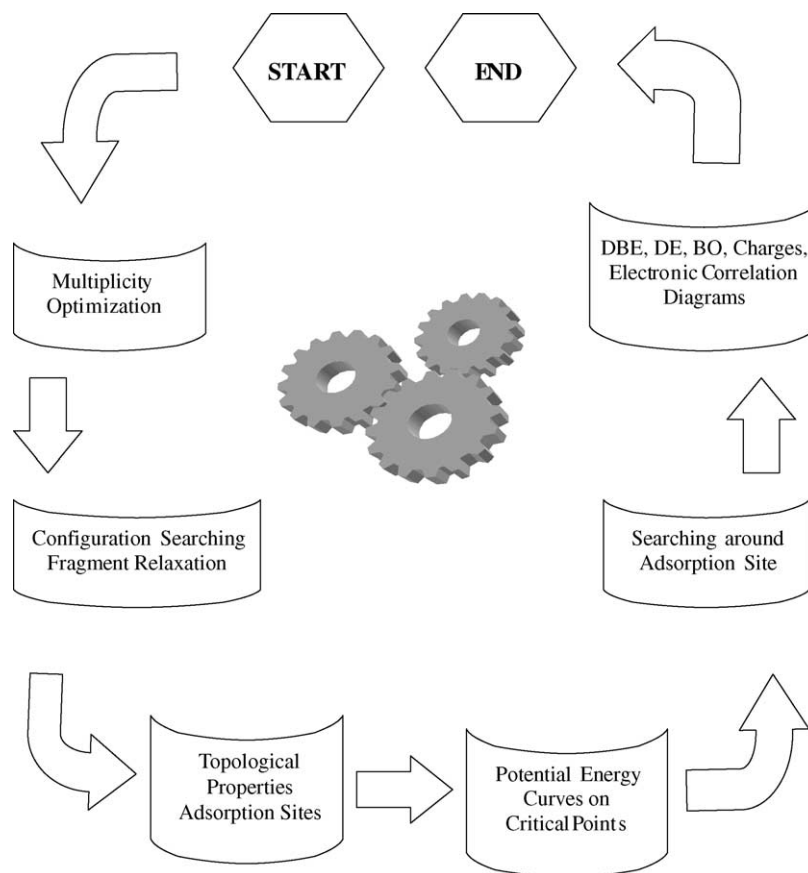


Fig. 5. Strategy employed in calculations of interaction adsorbate–substrate (adsorption process).

be calculated with relatively high accuracy by *ab initio* methods. On other hand, location of adsorption sites, intermediates, geometries, and possible products can be explored before doing ABQC. In particular, initial guest matrices from parametric methods can be the starting point in *ab initio* calculations of large systems.

Some of the ideas presented above have been implemented in our program CATIVIC [17,79–81]. This is the first version of a code specially tailored for catalytic reactions that offers several tools to facilitate their modeling. A schematic diagram for different stages in the calculation of the adsorption step is shown in Fig. 5. (a) Transition metal clusters normally have unpaired electrons; therefore automatic optimization of the substrate spin-configuration is performed for a selected range of multiplicities after geometry optimization, deciding on the most stable. (b) Several techniques have been implemented to find the most stable state and excited states associated with electronic configurations of the substrate and substrate–adsorbate system. Substrate density relaxation for prepared states and the possibility of electing different initial-guess configurations are accessible by considering only the shifting of molecular orbitals. (c) The location and properties of adsorption sites can be determined from the topological properties of the density Laplacian, as well as the optimal orientation of adsorbates on the surface [20,21]. Parametric

methods have demonstrated that it is possible to reproduce qualitatively *ab initio* theoretical results of valence critical points [82]. (d) The PEC is calculated by means of a scan along the line that joins the critical points of the adsorbate and substrate. (e) A scan in other directions is also performed in order assure the optimal interaction, relaxing at each point all the components of the system. (f) Bonding properties are evaluated considering diatomic binding energies (DBE) [83], diatomic energies (DE), bond orders (BO), charges, and molecular orbital correlation diagrams are computed [84] to discern adsorbate and substrate orbitals that participate in the adsorption bond.

The methodology for optimization of atomic and molecular parameters using standard parametric functionals are described elsewhere [79,85]. We are working on more sophisticated functionals that depend on functional expansions [78] and lead to a more involved reparameterization.

5. Parametric applications to catalysis

5.1. Size effect on zeolite adsorption site

There is experimental evidence of non-local, long-range interactions in the zeolite structure; for example, the acidity

changes with the Si/Al ratio [86]. It means that Al atoms, in spite of having long separation distances, maintain important interactions, and their presence influences the electronic charge concentration at other adsorption sites. Similar results were reported in previous work [79] with different clusters and smaller charged systems. In addition, long-range interactions in the computation of adsorbate–substrate interactions have been proposed to be relevant in molecular dynamics simulations [87]. These results are supported by a satisfactory comparison between CATIVIC and DFT calculations using a $\text{Si}_2\text{AlO}_4\text{H}_8\text{Fe}$ cluster [79].

The variation of charge dissipation with cluster size has a strong significance in the reactivity of the catalytic active site [88]. In addition, more realistic cluster size models are convenient because, in many cases, reaction products may be controlled by the size of the zeolite micro-cavities. Therefore, it would be important to understand the effect of a three-dimensional cavity on the active-site properties because the electric field generated by the adsorption site surroundings affects the kinetics and, consequently, the reactivity of the catalytic system especially for supports that display an ionic nature.

The effects of cluster size on the adsorption of a NO molecule on a metallic catalytic site of FeO-ZSM-5 zeolite were considered using several cluster sizes where a straight channel of a micropore formed by 10-rings with all adjacent 5- and 6-rings is simulated. The aim of this research is to confirm that the use of standard small clusters present important deficiencies in the representation of the catalytic active site. The use of parametric methods, such as CATIVIC, can be useful in such catalytic modeling. Calculated clusters of small, medium, and relatively big sizes were considered: $\text{Si}_2\text{O}_4\text{H}_8\text{AlOFe-NO}$, $\text{Si}_9\text{O}_{12}\text{H}_{20}\text{AlOFe-NO}$, $\text{Si}_{31}\text{O}_{43}\text{H}_{44}\text{AlOFe-NO}$, and $\text{Si}_{95}\text{O}_{157}\text{H}_{70}\text{AlOFe-NO}$ of 19, 46, 123, and 327 atoms, respectively (see Fig. 6). Edge Si atoms were saturated with H atoms. The first step was to optimize the H atoms keeping the rest of the system fixed. For the subsequent calculations, the H atoms were maintained unchanged in order to simulate the cluster surroundings due to the zeolite bulk. A total optimization was carried out for all systems without the adsorbate. Spin multiplicities of 1, 3, 5, 7, and 9 were evaluated for clusters without NO, being the multiplicity of 5 and then 7 the most stable ones. Then, local optimizations of Fe, all oxygen atoms bonded to Fe, and NO were performed for each cluster system after NO adsorption using a multiplicity of 4. The NO molecule is bonded through the N atom; however, adsorption of O atom is also feasible.

Qualitative information can be obtained from the charge changes in different atoms of the substrate and adsorbate. The charge differences between the A, B, C, and D models (see Fig. 6) with NO adsorbed and model A without NO are presented in Table 1. In all cases it may be observed that the Fe atom gains electrons with NO adsorption, and the charge change increases with model size. These results show a significant increase of the electronic density at the adsorption site. This is in agreement with other theoretical findings where the

Table 1
Charge changes on Fe, O, O*, N, and NO for models A, B, and C with NO

Model	Charge ^a (a.u.)					
	Fe	O _(zeo)	O [‡]	O*	N	N–O
A	0.24	0.06 0.01	0.01	0.26	–0.70	–0.44
B	0.28	0.06 –0.01	0.04	0.25	–0.63	–0.38
C	0.44	0.05 –0.02	0.07	0.25	–0.72	–0.47
D	1.21	–0.08 –0.14	–0.01	0.33	–0.94	–0.61

Positive values indicate that the electronic density increases in the corresponding atom. O_(zeo): oxygen of zeolite; O[‡]: oxygen only bonded to Fe; O*: oxygen of NO.

^a With respect to the model A without NO.

charge of the compensating cation is dissipated with cluster size [88]. The increase of the Fe electronic charge also correlates with the decrease of the Fe–O[‡] bond strength. For the zeolite oxygen atoms directly bonded to Fe, the changes are small. Similarly, the charge changes in the oxygen atom bonded to the iron (O[‡]) are unimportant. A different charge change (loss of electrons) is observed in the O and N atoms of NO. Adsorption of N–O produces an electronic charge withdrawal from N–O to Fe. The negative charge on the O* atoms seems to increase as the size of the substrate increases. On the other hand, the N atom losses electronic charge, and the largest charge reduction occurs in the D model.

Cluster-size effects may be analyzed by the study of the global softness ($S = 1/(IE - EA)$, where IE and EA are ionization energy and electron affinity of the system) [88]. Values of S are evaluated by considering the HOMO and LUMO energies for IE and EA, respectively. The calculated values of S for the A, B, C, and D models show a small increase with cluster size (3.33, 3.61, 3.60, and 3.64, respectively). The trend obtained by Chatterjee and Iwasaki [88] is similar, but their S value changes are higher probably due to the use of small cluster models.

5.2. Location of Al and Fe adsorption sites

The distribution of Al and Si in zeolite frameworks has a strong influence on their catalytic properties [89]. Unfortunately X-ray diffraction is not practical for the direct detection of Al locations on zeolites. A variety of studies using quantum methods have been carried out for the sitting of Al atoms on zeolites of the ZSM-5 type. Berán [90] using a semi-empirical method predicted the T12 and T2 sites. Blanco et al. [91] and Redondo and Hay [92] found that the site T9 is the most stable. Derouane and Fripiat [93,94] using a Hatree-Fock level of theory proposed the T12 and T2 sites on ZSM-5. On the other hand, Alvarado-Swaisgood et al. [95], using a HF method, reported that the most probable T sites occupied by Al are T6, T12 and T9, while Lonsinger et al. [96] found that Al in T12 site is the most energetically stable. Experimental results with X-ray diffraction using Cs

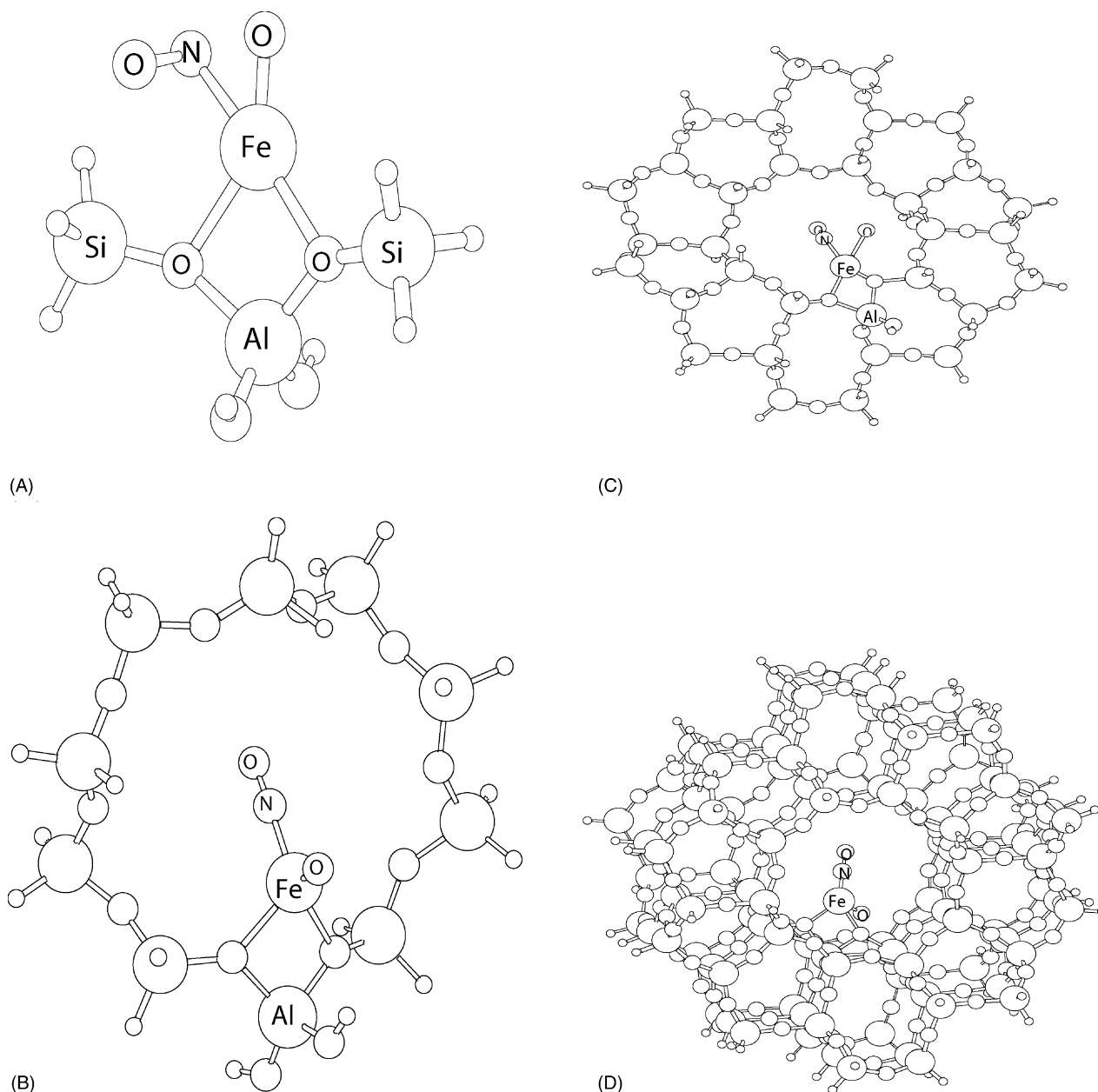


Fig. 6. Models of zeolite doped with FeO and NO chemisorbed: (A) $\text{Si}_2\text{O}_4\text{H}_8\text{AlOFe-NO}$; (B) $\text{Si}_9\text{O}_{12}\text{H}_{20}\text{AlOFe-NO}$; (C) $\text{Si}_{31}\text{O}_{43}\text{H}_{44}\text{AlOFe-NO}$; and (D) $\text{Si}_{95}\text{O}_{157}\text{H}_{70}\text{AlOFe-NO}$.

as charge-compensating cations [97] show that T6 and T9 sites are the most probable ones. Nevertheless, experiments with same technique [98] report that Al exchange is produced at the T12, T7 and T10 sites. It may be appreciated that both experimental and theoretical results are controversial.

All calculations for the location of the Al atom reported above were performed with small zeolite clusters. CATIVIC computations with a model cluster of 339 atoms ($\text{AlSi}_{79}\text{O}_{193}\text{H}_{66}$) of natural FMI zeolite known as mutinaite, with a similar structure of the synthetic ZSM-5, were carried out with a spin multiplicity of 2. At each T site, Si is replaced by Al without using a compensating cation. Total energy data for all 12 T different sites reveal that the most stable tetra-

hedral sites for Al sitting corresponds to T6 and T2 [99]. The zeolite cluster structure for these calculations is modeled with a sinusoidal channel that is similar to that presented in Fig. 7. This channel has been selected because it represents the most tortuous route through the zeolite, maximizing the contact time between reactant molecules and active sites.

A detail study of stability of Fe atoms in mutinaite on the sinusoidal channel was also evaluated for a similar industrial zeolite. Full optimization of all atoms, except edge H atoms, was carried out for the ($\text{FeSi}_{79}\text{O}_{193}\text{H}_{67}$) cluster of 340 atoms. All calculations were performed with a charge-compensating cation (H^+) located at the most stable place of the four oxygen atoms bonded to Fe at each T site. Results show that the H^+

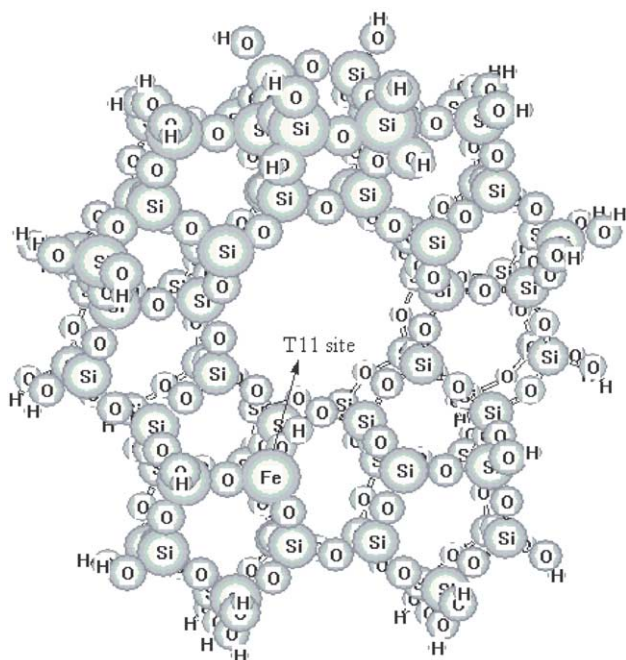


Fig. 7. Model of sinusoidal channel of a MFI zeolite (mutinaite) by a $XSi_{79}O_{193}H_{67}$ cluster ($X = Al$ and Fe).

location is at those sites that point toward the 10-ring channel. The optimal multiplicity for all systems was 6. Calculated total energy values show that the most stable sites correspond to T11 (see site presented in Fig. 7) and T5. One of these sites is also reported by Chatterjee and Chandra [100], using small clusters in a DFT approach, as one of the most stable (T11 and T3).

5.3. Extra-framework aluminium formation

Zeolite preactivation is generated by partial exchange of Na^+ by NH_4^+ and then steam calcination at $600^\circ C$. Theoretical and experimental determinations of active sites in zeolite frameworks are a controversial issue because preactivation can produce extra-framework aluminium (EFAL) [101]. Several authors suggest that there is a correlation between catalytic activity and the presence of non-framework Al active species [89,102–105]. In this subsection, we present the study of water molecules interactions around an Al site located on a 4-ring. These framework positions are under strain and are susceptible to undergo transformations as proposed by Kunkeler et al. [106] in zeolite beta.

A previous comparison of calculations for $Al(OH)_3H_2O$ and $Al(OH)_3(H_2O)_3$, using a first version of CATIVIC and an ab initio option (DFT-B3LYP/6-311G**) in Gaussian 98 [107], has been carried out. Results show longer values for Al–O and O–H average bonds (6% and 1%, respectively) in CATIVIC with respect to DFT values [108]. This means that qualitative results may be used to understand zeolite changes under hydrothermal treatment. Thus, calculations with small aggregates of 25 atoms ($AlSi_3O_{12}H_9$) that represent a 4-

ring in ZSM-5 zeolite have been performed, taking into account the interaction of a H_2O molecule with Al at different (H_2O)–Al distances. The formation of a penta-coordinate complex takes place because H_2O is bonded to Al. Using H_2O coordinates from the small aggregate into a larger cluster ($AlSi_{63}O_{152}H_{49}$) of 265 atoms, calculations were carried out and a similar complex is produced ($AlSi_{63}O_{152}H_{49}-H_2O$). An alike penta-coordinate intermediate has been proposed by Kunkeler et al. [106]. Nevertheless, the Al–O bond breaking occurs after the interaction with another H_2O molecule. Note that in all our calculations we do not consider temperature effects. The Al–O bond distances and Al–O–Si angles change with cluster size, even though in the small cluster the edge H atoms are maintained fixed. The Al–O (oxygen atom of water) bond distances have values of 2.34 and 2.16 Å; for Al–O (oxygen that contains H^+) they are 2.25 and 2.30 Å; and the average value for the rest of the Al–O bonds are 1.850 and 1.72 Å for small and large clusters, respectively. O–Al–O angles have a maximum change of 7° . However, O–Si–O angle is largely distorted by about 30° with respect to the initial geometry (obtained from experimental data) in both CATIVIC and the DFT-B3LYP/6-311G** approach.

As far as we know, the whole process of EFAL formation has not been modeled by quantum methods. The complete formation of EFAL was carried out with the $AlSi_3O_{12}H_9$ cluster as shown in Fig. 8. Successive water molecule ($6H_2O$) attacks to the Al–O bonds lead to the formation of different intermediate species (see a → f steps in Fig. 8). Bond distances and orders at each stage are shown in Table 2. The first step is the formation of a penta-coordinate species with the creation of an Al–OH₂ bond (see a). Breaking of the Al–O bond occurs after the formation of another Al–OH₂ bond (see b) keeping a penta-coordinate species but with two water molecules. The addition of another H_2O molecule forms an Al–OH and a SiO–H bonds, breaking a SiO–Al bond (see c). In the following step, a similar process occurs with the rupture of a third SiO–Al bond (see d). The scission of the last SiO–Al bond requires the formation of a hexa-coordinate species (see e); and then the sixth H_2O molecule produces an $Al(OH)_3$ species that is able to migrate through the zeolite channels. Partial results seem to indicate that a similar process occurs when using the 265 atoms cluster.

5.4. Prebiotic molecules on interstellar clusters of polycyclic aromatic hydrocarbons

Prebiotic molecular catalytic synthesis in the interstellar medium (ISM) is a very interesting and unexplored issue that is suitable for computational modeling. The presence of amino acids in meteorites [109,110] suggests an extraterrestrial origin of life [111]. Calculations with CATIVIC were carried out to study the formation pathways of amino acids, namely glycine and alanine, on the surface of the polycyclic aromatic hydrocarbon (PAH) coronene [112].

Parametric methods were selected because they are particularly helpful in the mapping out of reaction pathways

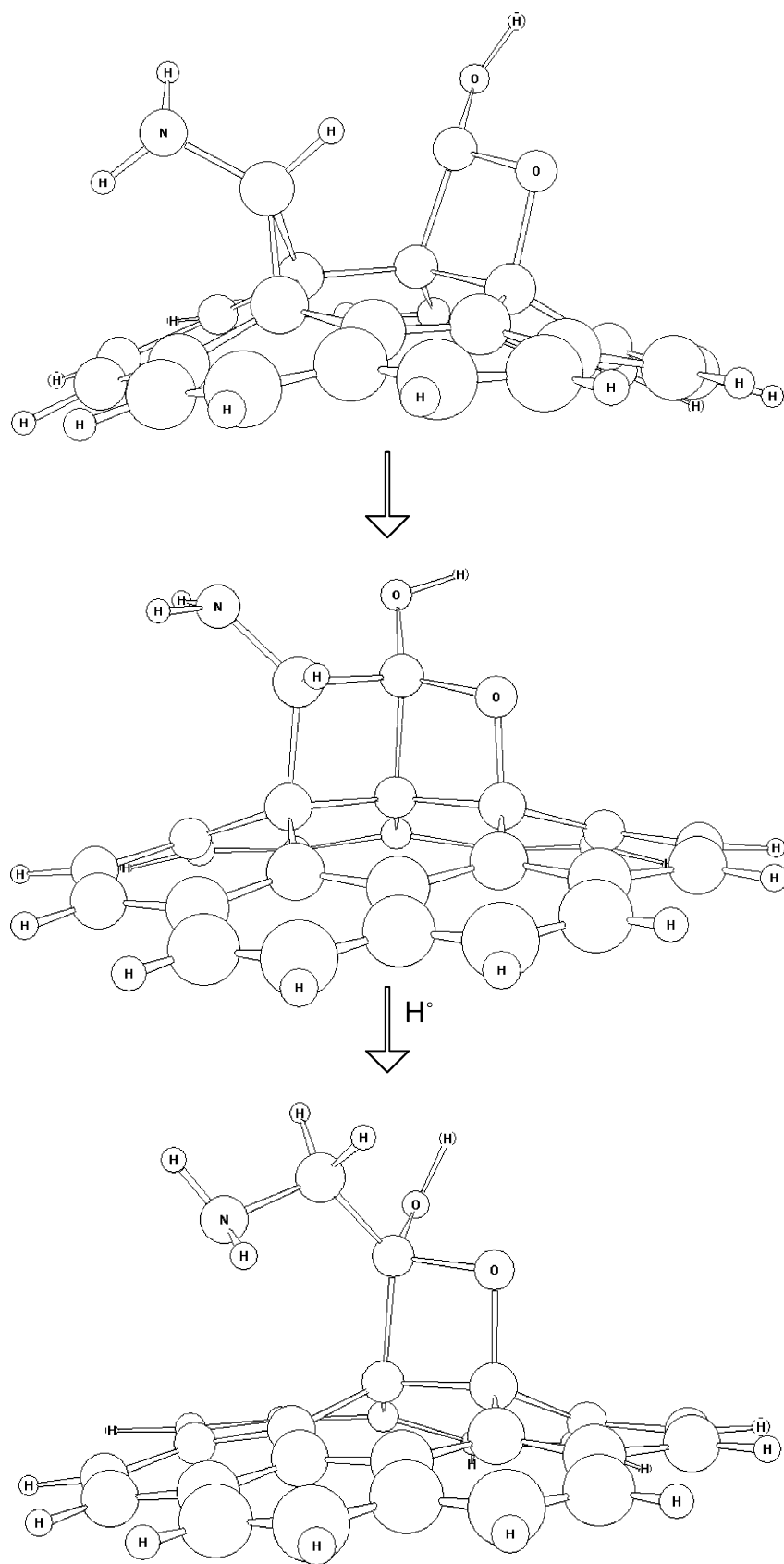
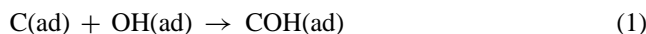


Fig. 9. Glycine formation on a PAH flake from adsorbed molecular fragments. Empty balls correspond to C atoms.

Amino acid formation may start with the formation of the carboxyl group (COOH) as previously proposed in the literature [113,114]. Calculations show that COOH can also be generated on PAH surface via the reactions

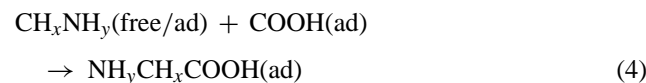


or

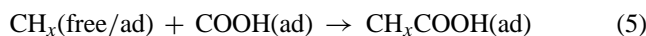


but these reactions are limited by surface diffusion constraints at low temperatures (10 K). The C and O atoms strongly chemisorb both on top of a substrate Cs atom (usually referred to as site A) and on the C_s–C_{s'} bridge (site B). Diffusion barrier between sites A and B was found to be less than 0.1 eV for both C and O adsorbates. Nevertheless, the differences in chemisorption binding energies ΔE_{AB} between A and B that can only be overcome by thermal hopping: for C, $\Delta E_{AB} = 1.74$ eV, and for O, $\Delta E_{AB} = 0.71$ eV. The OH radical chemisorbs only at A also with a strong binding energy of -2.62 eV. The key feature of reaction (2) is that the resulting CcOcoH adsorbate mode (to be referred hereafter to as M1) is chemisorbed to the surface through both Cc and Oc atomic components (see Fig. 9). Desorption energy barriers are around 0.53 eV, but the barriers for chemisorption from the gas phase are noticeably different at 2.94 eV. These barriers can be overcome in explosive events such as UV ice photolysis.

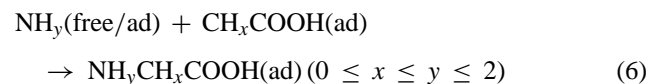
In agreement with Woon [114], we found that the formation of the CH₂NH₂ group is essentially the result of successive partial hydrogenations of CN; however, if *a-a* (adsorbate-adsorbate) and *f-a* (free-adsorbate) surface processes are invoked, hydrogenation may as well happen before and/or after C_α–N and C_c–C_α bonding (C_α is C in CH₂NH₂ and C_c is C in COOH). The *a-a* or *f-a* surface reactions of CH_xNH_y with M1 take the following steps:



(see Fig. 9); or alternatively,



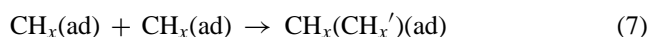
and then



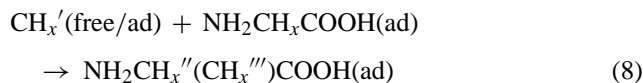
M1 adsorbate remains well anchored to the surface after reaction thus enabling further successive additions. It is worth mentioning that the formation of glycine from M1 is strongly competed: the single hydrogenation of M1 leads respectively to chemisorbed species of formic acid. Synthesis pathways involve chemisorbed CH_x and NH_y frag-

ments originating from ice photolysis or the hydrogenation of chemisorbed atomic species. For instance, CH, CH₂, and NH can chemisorb at both A and B sites with binding energy differences $\Delta E_{AB} < 0.33$ eV. However, there are always diffusion barriers between sites A and B; in this respect, the most mobile species is found to be CH₂ with $\Delta E_{AB} = 0.13$ eV and a diffusion energy barrier of 0.34 eV and a width at half maximum of ~ 0.29 Å which is susceptible to tunneling.

The surface synthesis of alanine proceeds in a similar fashion to that of glycine but a CH_x hydrogenation step is now replaced with the reaction



with $0 \leq x \leq 1$ and $0 \leq x' \leq 3$. A more efficient route would perhaps be the *a-a* recombination of CH_{x'} with a two-site chemisorbed amino-acid precursor:



where, for $0 \leq x \leq 1$ and $0 \leq x' \leq 3$, $x'' = x$ and $x''' = x'$, while for $x = 2$ and $0 \leq x' \leq 2$, $x'' = x - 1$, and $x''' = x' + 1$.

By comparing reactions on corenene and circumcoronene surfaces, significant model dependencies are encountered that indicate a preference for amino acid formation to occur on the smaller flakes due to a more extensive destruction of aromaticity by substrate reconstruction. It is also found that the chemisorption binding energies of the reacting and resulting adsorbates are significantly increased on the surface edge, a property that can lead to increased concentrations. In this situation, the two-site chemisorption of COOH imposes a strict handedness on amino acid formation that in the case of chiral surfaces can lead to enantioselection. Since graphitic surfaces are achiral, others attributed to interstellar grains, e.g. silicates, are being considered.

6. Conclusions and comments

- The importance of modeling catalytic systems is of high significance because the huge number of applications for catalysis in chemical manufacturing and in environmental and domestic use. This area deserves specialized software [19] for treating the multiple complex stages involved in surface catalytic processes.
- Modeling catalytic processes implies several theoretical branches of science and engineering and different time and space scales. A multidisciplinary approach is required to tackle the complexity of catalytic processes and the evaluation of micro and macro properties.
- Ab initio methods have become useful tools for predicting particular steps in catalytic processes, and a prominent future is foreseen for them mainly depending on the growth of computer capabilities. However, there is a lot of work to be done and challenging tasks lie ahead in or-

der to establish versatile ab initio approaches for tackling the difficult catalytic surface processes.

- (d) Among the alternatives that must be seriously considered are parametric methods. These methods are in their infancy because the systematic improving of parametric functionals is just starting. The precision of these methods depends on the reliability of the simulation techniques that are performed in the selection of elementary functionals and parameterization techniques. Application of a parametric method in catalysis with the code referred to as CATIVIC has shown several practical facilities that enable extensive calculations.
- (e) Qualitative information is very important from practical point of view. As mentioned by Reynolds [115], “Many industrial problems are simply too large for timely solutions using large-scale ab initio calculations . . . industrial chemists are often more interested in trends than absolute numbers.” The synthesis of catalysts requires inferences on structure, composition, effect of promoters, active sites, reactivity, stability, etc. prior to experimental design. There is no doubt on the importance of computational modeling in the very competitive area of new applications of catalytic devices using nanoparticles.

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