Chapter 1
Advances in Theoretical Studies on Solid Catalysts for Renewable Energy Production

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ABSTRACT

This chapter presents a brief review of the recent applications of the quantum chemical calculations in the catalysis for renewable energy production. In this, an introductory vision about the use of ab initio calculations in the field of the renewable energies is presented. It is worth mentioning that the quantum chemistry field is an extensive area with many methodologies and theoretical approaches; therefore, to shed some light on the application of this area on the catalysis for renewable energy production, the chapter is divide into two sections according to the employed theoretical approximation, that is, the cluster model approach and the periodic approach. The first section describes the cluster model approximation, followed by a discussion of recent works in hydrogen storage, biodiesel and methanol conversion fields, and the second section describes the basic principles of the periodic approximation, basis set used in this approximation, and illustrative examples in the catalysts for biodiesel production; reforming of methane and hydrogen storage are presented at the end of this section.

INTRODUCTION

The growing necessity of new renewable energy sources to substitute the fossil fuels has caused conjunction of different research areas among which the computational modeling and heterogeneous catalysis have played a crucial role. Heterogeneous catalysts help to transform the energy stored in a molecular structure to more accessible sources taking advantages of use a solid catalyst in the presence of the reactants in a liquid or gas phase e.g. hydrogen production from biomass by gasification process where dolomite and CeO_2/SiO_2-supported Ni, Pt, Pd, Ru, and alkaline metal oxides can be used to catalyze

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the gasification process (Tomishige, Asadullah, & Kunimori, 2004). The catalytic processes involve, in many cases, multiple individual reactions which make very difficult its optimization to reach the best performance of the catalytic system. It is in this point where the computational chemistry modelling helps to elucidate the intricate riddles that complex mechanisms in catalysis involve.

Computational simulations are the most significant developments in all the research areas in the last decades. There is in chemistry numerous methodologies and techniques that allow study from the interaction of two small molecules in gas state to the complex mechanisms involved in heterogeneous catalysis. From all methodologies developed in the computational chemistry field, the Density Functional Theory (DFT) has been used extensively in the last decades in chemistry simulations and its wide acceptance can be attributed to its reliability and low computational cost in comparison with other more expensive post Hartree-Fock methodologies. From its born with the Hohenberg-Khon theorems (Hohenberg, & Kohn, 1964) until today, the DFT methodology has reached levels where it is possible to attack with extreme reliability specific problems in the chemistry field as thermodynamic, kinetic and nonbonded interactions. This is thanks to the development of new functionals which have been parametrized and tested for these purposes. The functional is a fundamental part in the development of the DFT equations and involves all those necessary so that the density of a non-interacting electron gas reaches the exact behavior of the interacting electrons density in a molecular or solid system. Then, more sophisticated and labored functionals have been developed to increase performance of the DFT methodology which has caused its high popularity in the last years (Perdew, et al., 2005).

Since a heterogeneous catalytic reaction involves adsorption of reactants from a fluid phase onto a solid surface, from a computational modelling point of view the goal is built a reasonable model that correctly represent of surface and the catalyst active site. In general, there are two approximations to model a surface of a crystalline solid: by a finite number of atoms where the outer atoms are unsaturated and bond deficient or by a periodic approximation where the infinite repetition of a unit cell over the three coordinate axes simulates the solid periodicity (see figure 1). The main problem of the finite approximation (called cluster approximation henceforth) lies in the fact that unsaturated atoms of the model tend to be more reactive than the atoms of active site of the surface which leads incorrect interpretation of the active sites on the surface. This problem could be solved using a large number of atoms in the model which increases the computational cost. On the other hand, in a periodic approach the surface is simulated creating a vacuum in one direction of the solid. Due to infinite repetition of the cell, the vacuum produces two surfaces and the distance between both surfaces must be enough large to avoid interaction of the adsorbed molecule with both surfaces. Moreover, a small surface area of the unit cell

Figure 1. Representation of a Si surface model by: a) Cluster approach and b) periodic approach