Networked computing for ab initio modeling the chemical storage of alternative energy: Second term report (December 2015-February 2016)

Carles Martí (PhD student - ESR04), Leonardo Pacifici (Supervisor), Antonio Laganà (Supervisor) - Dipartimento di Chimica, Biologia e Biotecnologie, Università di Perugia, Perugia (IT)

Abstract

In this ESR04 second report the first steps of the approach followed to undertake the computational study of the kinetics of the H_2 + CO_2 Ni-catalyzed reaction are discussed. In particular my investigation is divided into two parts: a first dealing with the kinetic Monte-Carlo (kMC) simulation of the equations governing the production of CH_4 from CO_2 in the PROGEO apparatus and a second part related to possible improvements of the evaluation of the efficiency of the rate determining steps of the kinetic process by means of either quasi-classical, quantum-classical or full-quantum (even considering, when possible, on-the-fly methods) dynamics treatments based on high level ab initio electronic structure calculations of reactants, transition state and products. The report is preceded by a summary of the BSC Parallel Computing School attended in the 4th week of January.

Report

1) SCHOOL ON PARALLEL COMPUTING (BARCELONA 18-22/02/2016)

The school on parallel computing was held at the Barcelona Supercomputing Center (BSC) between 18-22 of January. The school was divided into three parts:

1. <u>MPI Programming</u>: In the first part of the school the parallelizing strategies based in distributed memory computing and its most popular standard, the Message Passing Interface (MPI), were explained. MPI defines the semantics of the use of a collection of library routines implemented in the most popular scientific programming languages (eg. Fortran, C/C++ and Java) with specific compilers. The design of MPI leverages on the parallelization paradigm of a

cluster of processors distributed on different computing nodes (each one with its own local memory and access) communicating by sending and receiving messages. The classes were divided into lectures (during which the key concepts of the message passing and the syntax of MPI calls were illustrated) and hands-on sessions (during which the concepts illustrated by the lecturer were applied to different types of routines).

2. <u>OpenMP Programming</u>: In contrast with MPI, the OpenMP (which stands for Open Multi-Processing) multiplatform API is based on a shared memory parallelizing paradigm. Different processors have access to a common memory whose blocks are shared (i.e. processors the on same node). The coordination is achieved by reading and writing into the common blocks. Programming languages for which OpenMP is available are Fortran, C/C++. The classes were divided into lectures (during which the syntax of the most popular standard (OpenMP) strategies and common problems like data race where treated) and hands-on classes in which the illustrated concepts were applied to common problems.

   <u>Combined OpenMP + MPI Programming and usage of analysis tools:</u> In this last part, topics regarding hybrid shared and distributed memory based strategies were given with the two most common standards. The lecture was completed by a hands-on session during which two analysis tools developed at the BSC, “paraver” and “tareador” were used. The first one is a group of tools allowing the analysis of the performance of a parallel program. It shows graphically, among other statistics, the work distribution among processors, memory distribution when distributed memory scheme is used and the load of the parallelization routine to create tasks. The second one shows, both numerically and graphically, how a sequential program is organised in order to ease its parallelization and to write performing parallel codes.

2) GEMS: THE GRID EMPOWERED MOLECULAR SIMULATOR

Work on the kinetic simulation has been started by trying to extend the Grid Empowered Molecular Simulator (GEMS) [1] procedure (designed and developed in the Computational Dynamics and Kinetics (CDK) laboratory of the University of Perugia in which I am presently working) to the *ab initio* simulation of non elementary chemical processes. The critical steps of the simulation extend over different time scales of not only generating high level *ab initio* electronic structure information and handling the differential equations of the nuclei motion but also integrating the kinetic equations of the intervening species.

The first module of GEMS (INTERACTION) targets the collection and, where necessary, also the afresh production of the electronic structure information of the molecular system of the considered elementary process(es) at different levels of theory. This approach, in contrast with direct (on the fly) ones, allows not only the reuse of the outcomes of previous investigations but also the correction of non converged data. For this reason, before starting new production runs of *ab initio* electronic energy values, I carried out a search for electronic structure data available from the literature of publically available databases [2] including those obtained by a rationalization of experimental data. In some cases the information was completed by resorting into afresh runs of high level *ab initio* calculations aimed at building either local or extended sets of electronic energy values depicting in detail the shape of the regions of the Potential Energy Surface (PES) of interest for the calculation. The calculations of the INTERACTION module can be run concurrently on a Distributed Computing Infrastructure (DCI) [3] exploiting the highest level possible of theory on an appropriate grid of molecular geometries using the most suitable (at least "de facto") standard data format in order to facilitate the merging of electronic structure information obtained from different sources. The gathered data are then fitted to a suitable functional form to generate an analytical PES in the second module of GEMS (called FITTING) that allows to operate on the *ab initio* values to depurate them of possible errors and inconsistencies. The PES obtained in this way is then passed to the third and fourth modules of GEMS (DYNAMICS and OBSERVABLES, respectively) calculating the efficiency of the considered processes.

3) THE KINETIC MODEL OF THE H_2 + CO_2 SYSTEM

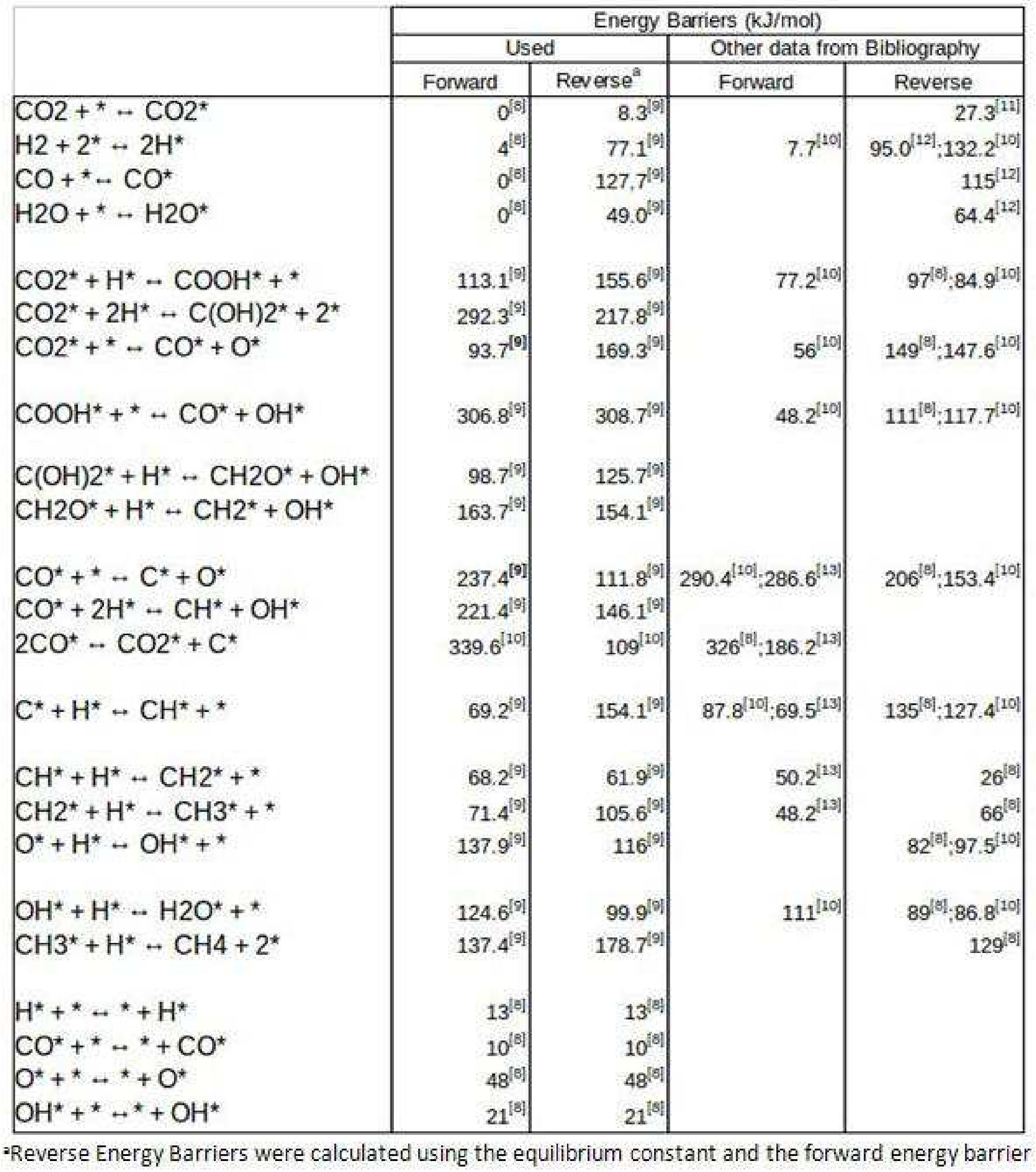
In order to handle the kinetic model of the H_2 + CO_2 system, use has been made of ZACROS [4] a Kinetic Monte Carlo (KMC) [5,6] software package written in Fortran

2003, for simulating molecular phenomena on catalytic surfaces [7] leveraging on the Graph-Theoretical KMC methodology coupled with cluster expansion Hamiltonians for the ad-layer energetics and Brønsted-Evans-Polanyi relations for the activation energies of elementary events [5]. ZACROS enables researchers in the areas of Computational Catalysis and Surface Science to perform dynamic modeling of adsorption, desorption, surface diffusion and reaction processes on heterogeneous catalysts. The rates of these elementary processes are expected to be computed from first principles (*ab initio*) so as to enable the prediction of catalytic performances (such as activity and selectivity). The package can also perform simulations of desorption/reaction spectra at a given temperature providing so far a rationale for designing kinetic mechanisms and supporting them when carrying out a comparison with experimental data.

The ZACROS framework can naturally capture:

- Steric exclusion effects for species that bind in more than one catalytic sites.
- Complex reaction patterns involving adsorbates in specific binding configurations and neighbouring patterns.
- Spatial correlations and ordering arising from adsorbate lateral interactions that involve many-body contributions.
- Changes in the activation energies of elementary events, influenced by the energetic interactions of reactants with neighbouring spectator species.

The elementary processes considered for our simulations are given in the leftmost column of Table 1.



	Energy Barriers (kJ/mol)			
	Used		Other data from Bibliography	
	Forward	Reverse[a]	Forward	Reverse
CO2 + * ↔ CO2*	0[8]	8.3[9]		27.3[11]
H2 + 2* ↔ 2H*	4[8]	77.1[9]	7.7[10]	95.0[12];132.2[10]
CO + * ↔ CO*	0[8]	127,7[9]		115[12]
H2O + * ↔ H2O*	0[8]	49.0[9]		64.4[12]
CO2* + H* ↔ COOH* + *	113.1[9]	155.6[9]	77.2[10]	97[8];84.9[10]
CO2* + 2H* ↔ C(OH)2* + 2*	292.3[9]	217.8[9]		
CO2* + * ↔ CO* + O*	93.7[9]	169.3[9]	56[10]	149[8];147.6[10]
COOH* + * ↔ CO* + OH*	306.8[9]	308.7[9]	48.2[10]	111[8];117.7[10]
C(OH)2* + H* ↔ CH2O* + OH*	98.7[9]	125.7[9]		
CH2O* + H* ↔ CH2* + OH*	163.7[9]	154.1[9]		
CO* + * ↔ C* + O*	237.4[9]	111.8[9]	290.4[10];286.6[13]	206[8];153.4[10]
CO* + 2H* ↔ CH* + OH*	221.4[9]	146.1[9]		
2CO* ↔ CO2* + C*	339.6[10]	109[10]	326[8];186.2[13]	
C* + H* ↔ CH* + *	69.2[9]	154.1[9]	87.8[10];69.5[13]	135[8];127.4[10]
CH* + H* ↔ CH2* + *	68.2[9]	61.9[9]	50.2[13]	26[8]
CH2* + H* ↔ CH3* + *	71.4[9]	105.6[9]	48.2[13]	66[8]
O* + H* ↔ OH* + *	137.9[9]	116[9]		82[8];97.5[10]
OH* + H* ↔ H2O* + *	124.6[9]	99.9[9]	111[10]	89[8];86.8[10]
CH3* + H* ↔ CH4 + 2*	137.4[9]	178.7[9]		129[8]
H* + * ↔ * + H*	13[8]	13[8]		
CO* + * ↔ * + CO*	10[8]	10[8]		
O* + * ↔ * + O*	48[8]	48[8]		
OH* + * ↔ * + OH*	21[8]	21[8]		

[a] Reverse Energy Barriers were calculated using the equilibrium constant and the forward energy barrier

TABLE 1 – List of the elementaryprocessesconsidered for the Ni-catalyzedreduction of CO$_2$ to CH$_4$ (leftmostcolumn). In the centralcolumns the activationenergies of the direct (first column) and of the reverse (secondcolumn) processesare given. Relatedreferences are given in the rightmostcolumns.

4) THE EVALUATION OF THE RATE COEFFICIENTS

In kinetic simulation packages the rate coefficients of the intervening elementary processes are usually expressed in terms of Transition State (TS) theory (ie. as the product of a pre-exponentialfactor (let us call it A) by an exponential term). The two terms refer to an intermediate molecular geometry of the system associated with the TS that is assumed to separate reactants and products along a properly chosen coordinate (reaction coordinate). Moreover, once crossed the TS is assumed not to be recrossable back. Empirical corrections to the TS are given by a mitigation of the no-recrossing assumption and by the introduction a steric factor in order to account for an angle of attack dependence of the reaction probability.

The exponential term is usually expressed as e^{-E_p/k_BT} that incorporates the information on the PES of the related elementary process p (for the direct or forward “f” and for the reverse or backward “b”) for which E_p, is the difference between the energy associated with the stationary point of the potential Minimum Energy Path (MEP) at the transition state and that associated with the original asymptote of the process.

In low level approximations, the pre-exponential factor can be given by the simplified expression k_BT/h where k_B is the usual Boltzmann constant, while T is the temperature and h the Planck constant.

A more accurate formulation of the rate coefficients makes use of the partition function of the intermediate state (incorporating so far the information about the remaining degrees of freedom):

$$A = \left(\frac{k_BT}{h}\right)\left(\frac{Q^{TS}(Q'_{slab})^{R_{tot}-1}}{\prod_{r=1}^{R_{tot}} Q_r}\right)$$

where Q^{TS} is the transition state partition function, Q'_{slab} the partition function of the metallic surface and Q_r the partition function of adsorbed species.

Each partition function is calculated considering that rotations and translations are frustrated or hindered and therefore can be assimilated to vibrational degrees of freedom. In that case, the vibrational partition function takes the form:

$$Q_{vib,X} = \prod_k \frac{exp(\frac{-h\nu}{2k_BT})}{1 - exp(\frac{-h\nu}{k_BT})}$$

Where $Q_{vib,X}$ is the total vibrational partition function of the species X, k refers to the vibrational normal modes and ν is the vibrational frequency of normal mode k.

A comparison of the methods illustrated above is given below

In order to illustrate how the ZACROS code works the Ziff-Gulari-Barshad Model (ZGB) [14] bench case taken from its Tutorial section has been considered (see ref. 4). The ZGB bench case models the catalyzed oxidation of CO by O_2 using three simple and irreversible elementary steps:

1. CO adsorption
2. O_2 dissociative adsorption to 2O
3. CO+O desorption reaction

Despite its simplicity, the ZGB case serves perfectly to the end of introducing the key features of data handling of the code and of the operations performed during the simulation.

The input to the program consists of four mandatory files and an optional one:

- `simulation_input.dat`
- `lattice_input.dat`
- `energetics_input.dat`
- `mechanism_input.dat`
- `state_input.dat` (optional).

In the first file simulation the main simulation parameters are passed to the program, including random seed, temperature, pressure, gas species general info, adsorbed species general info, writing frequency of output data, stopping criteria and debugging parameters.

In the second file `lattice_input.dat` the information regarding the lattice structure and different types of sites within the lattice are provided (either default or custom lattice structure can be chosen). Hexagonal periodic default lattice will be the one of our choice for the ZGB model as well as for the Sabatier process.

As mentioned before, the ZACROS code is based on a cluster expansion Hamiltonian definition. This information is provided in the third file (`energetics_input.dat`). The file is divided into clusters of atoms in which information regarding number of sites, its neighboring, energetics etc. are provided.

The `mechanism_input.dat` file is the one in which all elementary steps information are introduced. The file is made of a sequence of steps, without any specific order. Information about step reversibility, activation energies, pre-exponential factors and variation of gas and adsorbed species are introduced in the file.

Data used by us for the ZGB model calculations can be obtained from the ZACROS webpage. Related results are illustrated in Figure 1.

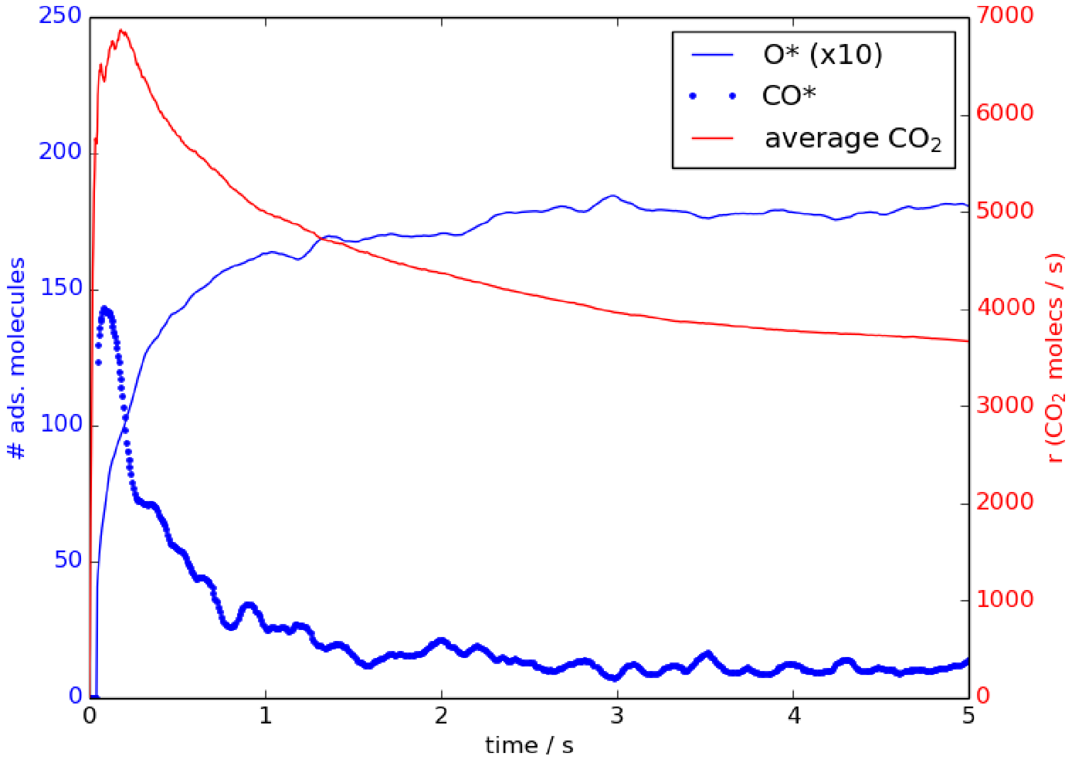


Figure 1. Plots of the produced number of CO_2 molecules per second (red, right axis), adsorbed CO molecules (dotted blue line, left axis) and the O adsorbed adatoms x 10 (solid blue line, left axis).

Figure 1 shows how CO_2 production rate raises until a maximum at ~0.25 s following by an asymptotic decrease. This fact can be explained considering the fact that O* is thermodinamically more stable than CO* but its formation activation barrier is higher having this way a slower production rate. Over time O* displaces CO* from surfaces resulting in a maximum CO_2 production rate when the two concentrations are equal (and the product of coverages is maximized). After that, O* acts partially as a poison for the surface letting CO* have only a small coverage, and hence CO_2 production rate decreases until the steady state is reached.

4) THE DYNAMICAL CALCULATION OF THE RATE COEFFICIENTS

As already mentioned accurate evaluation of the rate coefficients can be obtained from dynamical calculations. For this reason we plan to activate related programs in the simulator. The most popular dynamical approach to the calculation of bimolecular collision rate coefficients is the one integrating classical mechanics equations, implemented into the VENUS code. which has been extensively used for a variety of calculations [15-21].

By continuing along the line illustrated in the previous report we discuss here the quantum classical code (QCMET) developed by G. Billing and C. Coletti [22], adopting a quantum description of the vibrational degrees of freedom and a classical one for the others. This method brings into trajectory calculations quantum effects typical of vibrations (zero point, interference and resonance effects) and is particularly useful when dealing with many degrees of freedom. To this end I paid a one week visit to the University of Chieti in the group of C. Coletti with whom I started the activation of the program. For the study two kinds of simulations: the state specific reactive scattering (see eq. 1) and the non-reactive scattering (see eq. 2) for the following diatom-diatom processes:

$$AB_{(v1,j1)} + CD_{(v2,j2)} \longrightarrow ABC + D \qquad \text{Eq. 1}$$

$$AB_{(v1)} + CD_{(v2)} \longrightarrow AB_{(v\prime 1)} + CD_{(v\prime 2)} \qquad \text{Eq. 2}$$

have been considered. Once set the initial conditions (impact parameter, intermolecular distance, the three angles and vibrational (v_i) and rotational (j_i) quantum numbers and translational energies) the time integration is performed. When finishing conditions are reached the program calculates state specific reactive probabilities $P(v_i, j_i)$ and reactive cross sections $\sigma(v_i, j_i)$. The program computes a state specific reactive probability by computing difference between initial and final norm of reactants' wave-function. The final reactivity is calculated by averaging reactive probabilities associated with a fairly large number of trajectories. During my visit the program was tested by performing some calculations for the CN + H_2 system.

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