Simulation of methane production from carbon dioxide on a collaborative research infrastructure

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Abstract. We have implemented the numerical simulation of the kinetics of the Ni-catalyzed $H_2 + CO_2$ process to assist the development of a prototype experimental apparatus producing methane. To this end the simulation program has been ported onto the segment of the distributed platform available to the Virtual Organization COMPCHEM as part of a set of use cases gathered to the end of establishing a European Research Infrastructure. The model adopted, the structure of the software and its parallel reorganization are discussed by taking as a reference the present working conditions of the apparatus in its location at the University of Perugia.

Keywords Sabatier reaction, kinetic model, concurrent computing.

1 Introduction

The present trend of chemical research and, as a consequence, of computational chemistry activities is increasingly moving out from purely *per se* theoretical investigations into service oriented ones meeting societal challenges. In this perspective our research laboratory has taken part into a joint private-public effort to build PROGEO 20 kW, a prototype apparatus based on a Power-to-Gas technology for electricity storage and CO_2 valorization. PROGEO 20 kW is an innovative electricity storage apparatus, based on the conversion of low cost (or not to produce in order to avoid instability in the electric network) electricity into methane through a high efficient process made of:

- an electrolyzation stage in which electricity is converted into high purity hydrogen (H_2);
- a methanation stage in which hydrogen reacts with carbon dioxide (CO_2) to produce methane and steam water.

Due to the exothermic nature of the reaction, the setup requires a negligible additional energetic cost to be self-sustained. Moreover, CO_2 is a by-product of several processes and, consequently, it is interesting to consider it for recycling. The PROGEO apparatus has also the following positive additional characteristics:

- a fast start-up thanks to a highly flexible solution (patented);
- the possibility of being used for feeding both electrical and methane distribution nets;
- a great safety level thanks to an intrinsically passive control system (patented);
- an extremely large number of charge/discharge cycles;
- a modular integrability in stacks.

The apparatus, designed by Andrea Capriccioli, has been assembled at the PLC System s.r.l. an international company operating as supplier of electrical power. In particular, the company is specialized in designing, installing and monitoring energy supplying apparatuses (both from fossil and renewable sources). PROGEO is likely to become, in the near future, a product to offer to its customers. PROGEO 20 kW, in fact, targets a low level user who wishes to combine cheap energy (saving on its cost) with CO_2 recycling (saving on carbon tax) for its own business. However, the next planned PROGEO apparatus is PROGEO 0.5 MW more targeted to industrial applications (though still being a prototype experimental one) suitable for coupling with small power plants. [1]

The increasing involvement of different expertise in the scale up of the applications (as is the mentioned increase in power from 20 to 500 kW and the already planned further upgrades) has originated from the synergy between research and infrastructural activities fostered by the forming of Virtual Organizations (VO) [2] and Virtual Research Communities [3] promoted by the EGEE (Enabling Grids for E-Science in Europe [4]) and EGI (European Grid Infrastructure) [5] calls (in particular, the COMPCHEM VO [6] and of the Chemistry, Molecular & Materials Science and Technology (CMMST) VRC [7] in the field of Molecular Sciences and Technologies (MST). The COMPCHEM VO, first, and (with a wider participation) the CMMST VRC, later, were in fact established with the specific purpose of supporting collaborative computational chemistry applications by both sharing grid resources and workflowing different competences and codes (more details will be given in Section 2). Along this line of action in order to create a more solid ground for collaborative research and innovation, jointly with the computer centres of Westminster (UK) and Tubingen (DE) and the cooperation of other institutions and companies, we assembled a proposal for the "INFRAIA-02-2017: Integrating Activities for Starting Communities" call aimed at establishing an MST Research Infrastructure (RI). The proposal [8], named Supporting Research in Computational and Experimental Chemistry via Research Infrastructure (SUMO-CHEM), addresses several societal challenges among which the storage of renewable energies as chemical energy and, in particular, as CH_4 (Power-to-gas) that is the goal of the PROGEO apparatus.

In this paper we report, indeed, on the first implementation of the numerical simulation (developed in parallel with the assemblage of the experimental apparatus) designed for the rationalization of the methanation process of PROGEO. Accordingly, in Section 2 we discuss the frame of the proposed MST RI;

in Section 3 we describe in some detail the structure of the simulator of the Sabatier Ni-catalyzed carbon dioxide reduction to methane of PROGEO;

in Section 4 we analyse the outcome of the simulations and we infer some features of the reactive mechanism;

in Section 5 we present some indications on future work.

2 The Molecular Science and Technology Research Infrastructure

The main aim of the proposed MST RI is to integrate Molecular Science research facilities, Technology infrastructures and e-infrastructure resources to the end of enabling synergetic Computational and Experimental Chemistry joint endeavours targeting some primary societal challenges. This implies, in fact, not only the provision of the know how for an intuitive and seamless access to advanced experimental and compute facilities but also for the utilization of high level of theory multiscale computer simulations and their coordination with experimental outcomes. Crucial in both respects is the shared and efficient management of data including its creation, publishing, accessing, curation and preservation using metadata and ontologies based on advanced services. For this purpose, significant efforts need to be spent to articulate the produced knowledge for an optimal use by both academia and industry.

Experimental raw data is expected to be generated by different experimental apparatuses. The wider range of MST experimental apparatuses is that related to measurements of properties related to light-matter interaction. The top ranking type of experimental apparatuses involved in the proposal are Synchrotrons and Lasers (in particular those of the Trieste European facility: the Elettra synchrotron and the Fermi free-electron laser). At Elettra all of the most important X-ray based techniques are available, as well as facilities for infrared microscopy, spectroscopy or ultraviolet scattering. FERMI is a single pass seeded FEL light source delivering ultra-high brilliance, fully coherent, ultra-short UV and X-ray pulses from the UV down to ∼4nm. The two light sources allow to characterize material properties and functions with sensitivity down to molecular and atomic levels, to pattern and nanofabricate new structures and devices, and to develop new processes. The light source and the available experimental stations offer unique opportunities for exploring the structure and transient states of condensed, soft and low-density matter using a variety of diffraction, scattering and spectroscopy techniques. In addition the ultrafast lasers of the University of Madrid CLUR partner of the project provides the members of the proposal with high power lasing combined with multi-photon ionization spectroscopy and time-of-flight mass spectrometry. These research facilities also allow manipulation of materials (laser micro-fabrication, laser modification of materials, laser ablation) and the synthesis of new materials. They also allow to investigate laser-induced plasma and phenomena under non-equilibrium conditions. In addition FLASH (the Free-Electron LASer for VUV and soft X-ray radiation in Hamburg operated in the "self-amplified spontaneous emission" (SASE) mode and currently covering a wavelength range from 4.2 nm to about 45 nm in the first harmonic with GW peak power and pulse durations between 50 fs and 200 fs), PETRA (the accelerator of the DESY site in Hamburg now operating as the most brilliant storage ring based X-ray source worldwide enabling Pump-probe X-ray absorption experiments with high photon flux in the energy range of 50-150 keV that can be performed on it in a 40-bunch mode) and LENS (the European Laboratory for Non-linear Spectroscopy, providing short-pulse lasers as experimental facilities for spectroscopic and non-linear optics research with frequency domain from the far IR to the extreme UV with the highest available resolution, with a time domain ranging from few femto to nanoseconds, allowing running time-resolved spectroscopic experiments such as degenerate and non-degenerate four wave mixing experiments (photon echo, optical Kerr effect, transient gratings, etc.), time resolved fluorescence, two-dimensional infrared spectroscopy, transient absorption and stimulated emission and multi-photon spectroscopy) are also other examples of the invaluable light-matter experimental machinery of the proposed European MST RI.

The second set of MST experimental apparatuses involved in the proposal are those producing raw data related to matter-matter interaction. Typical instrumentation of this type are the molecular beam-molecular beam or -gas collision apparatuses. Molecular Beams Laboratories can provide velocity, internal state, angular momenta dependence (in addition to mass spectrometric and time of flight) selected for reactants, products and transient analysis for single collision processes. This allows to estimate the value of the transition matrices, evaluate the role played by the reaction intermediate, validate the formulation of the molecular interaction and propose a process mechanism for different collision and internal energy values. More averaged, though spanning larger ranges of energy, are the experiments carried out for gas phase plasmas, combustion and biomasses. Related facilities support research on the formation and exploitation of oil, the design and implementation of advanced engines, the thermochemical conversion of biomasses, the combustion through chemical looping, the processes for transforming and storing energy. Moreover, laser-induced plasma and phenomena under non-equilibrium conditions provide information on the efficient use of energy in technological applications, such as negative ion sources for nuclear fusion, material science for aerospace and microelectronics applications, plasma-based energy recovery devices as well as micro-discharges for active flow control, and material synthesis and characterization.

The third set of raw data is obtained by more commercial apparatuses of large use by scientific laboratories and institutions like NMR, HPLC, X-ray, spectroscopes, etc. or assemblages of various types of this kind of equipments like burners, reactors, heat exchangers, etc. plus some *ad hoc* designed pieces as is the case of the already mentioned PROGEO object of our investigations.

The resulting layer of raw data resources will have to be made available in a proper (even if only *de facto*) standard format to researchers access through a science gateway. The science gateway will not only enable researchers to access research facilities, computing and data resources allowing experimental chemists to run experiments on remotely available research facilities but it will support also training activities, community building, and especially designed data services to run simulations through the submission service using different types of data resources (such as data archives, databases, data collections, data storages) and workflows.

The above given picture of the experimental facilities belonging to the MST RI will allow to manage extended libraries of computational applications covering the real Virtual Laboratories programs. Invaluable to this end is the extensive use of the computational resources and innovative on-line services of the EGI cloud and grid resources and of some partners like ENEA (CRESCO). This platform provides a unified user environment and a seamless user-friendly access method to combine computing resources and experimental facilities. It provides a unified user environment and a seamless user-friendly access method to combine computing resources and experimental facilities irrespective of their location. Similar support is planned to be given by MoSGrid the compute infrastructure configuring and providing Grid services for molecular simulations leveraging on an extensive use of D-Grid Infrastructure for high-performance computing. It includes metadata and their provision for data mining and knowledge generation. MoSGrid aims at supporting the users in all fields of simulation calculations. Via a portlet, the user can access data repositories where information on molecular properties as well as on "recipes" - standard methods for the provided applications are stored. By means of these recipes simulation jobs can be automatically generated and submitted into the Grid (Pre-processing and Job Submission). Moreover, the users are supported at the analysis of their calculation results. Through the cross-referencing of different result data sets, new insights can be achieved. The data repository additionally allows external referencing of simulation results. Further compute support will be provided from ReCaS (a cluster of 4 national Italian data centres (Napoli, Bari, Catania, Cosenza) of the national Italian Grid Infrastructure (IGI) that is part of the European Grid Infrastructure (EGI) and INFN. The key users are the research institutions in southern Italy regions and CERN (ATLAS, CMS, ALICE, LHCb). In addition to the mentioned compute infrastructures the following centers (EGI Federated Cloud and Grid, CINECA, PRACE, CRESCO, ZIH, some national and regional computer centres, openstack clouds, computer clusters, etc.) provide also compute support. As to the libraries of computational applications, the most popular of them are the *ab initio* simulation software packages such as ADF[9], DALTON[10], MCTDH[11], NWCHEM[12], etc. running on high performance computing resources, *ab initio* and density functional electronic molecular structure calculations using electronic structure calculation software (MOLPRO[13], MOLCAS[14], GAUSSIAN[15]) and dynamical calculation software (ABC[16], HYBRIDON[17], VENUS[18], QCTUCM[19]). Other in-house, open source or commercial codes available for use in the MST RI are: BTE (Boltzmann Transport Equations), DSMC (Direct Simulation Monte Carlo), PIC (Particle-in-Cell), PLASMA-FLU (plasma simulation), EPDA (Elementary Processes Data Aggregator), ORCA, Jaguar, MOPAC, DFTB+, MNDO99, QM/MM, CRECK, Pope, ANOVA, EVB (Empirical Valence Bond), MOLARIS, Q depending on the needs of different experiments (we refer here to the list given).

3 The PROGEO simulation

As mentioned above, our approach to the PROGEO simulations has been already designed along the guidelines of the CMMST VRC on which also the MST RI is being built using its compute platform.

In particular, the simulation of the methanation process of PROGEO was assembled starting from the already established Grid Empowered Molecular Simulator (GEMS) [20] used in recent times to carry out the OH + CO reaction virtual experiment whose products had been measured in a crossed beam experiment [21]. In the latter case the workflow was articulated in the following modules:

a) INTERACTION: devoted to the calculation of the electronic energies of atomic and molecular aggregates of the considered system using high level *ab initio* methods (was not used by us due to the fact that potential energy routines were already available from the literature);

b) FITTING: devoted to the fitting to a suitable functional form of the electronic energy values available for the system of interest and to the assemblage of an analytical formulation of the Potential Energy Surface (PES) (was not used by us due to what has been mentioned above);

c) DYNAMICS: devoted to the integration of the equations of motion for the nuclei of the system with initial conditions adequate to reproduce the experimental situation (was used by us to perform extended quasiclassical trajectory calculations mimicking the internal and collision energy distributions of the experiment);

d) OBSERVABLES: devoted to the averaging over the unobserved parameters of the product pulses counted by the detector and properly transformed, thanks to the knowledge of the geometry of the apparatus, into the value of the cross section and of the angular and translational distributions.

To the end of simulating the processes occurring inside the PROGEO methanator, however, we have further articulated the OBSERVABLES module so as to incorporate the time evolution of the kinetics of the interleaved elementary processes. For this purpose, we extended the above described GEMS schema to the simulation of the PROGEO methanator both

- by introducing the integration in time of the system of the kinetic equations intervening in the process of forming CH_4 from H_2 and CO_2 over Ni (111)

and

- by considering as part of the kinetic system all the processes related to the interaction of the involved atoms and molecules with the surface of the catalyzer (see the leftmost column of Table 1).

Step	$\mathbf{E}_a$ forward (kJ/mol)	$\mathbf{E}_a$ reverse (kJ/mol)
$CO_2 + * \leftrightarrow CO_2*$	0.0 [22]	8.3 [23]
$H_2 + 2* \leftrightarrow 2H*$	4.0 [22]	77.1 [23]
$CO + * \leftrightarrow CO*$	0.0 [22]	127.7 [23]
$H_2O + * \leftrightarrow H_2O*$	0.0 [22]	49.0 [23]
$CO_2* + H* \leftrightarrow COOH* + *$	113.1 [23]	155.6 [23]
$CO_2* + 2H* \leftrightarrow C(OH)_2* + 2*$	292.3 [23]	217.8 [23]
$CO_2* + * \leftrightarrow CO* + O*$	93.7 [23]	169.3 [23]
$COOH* + * \leftrightarrow CO* + OH*$	306.8 [23]	308.7 [23]
$C(OH)_2* + H* \leftrightarrow CH_2O* + OH*$	98.7 [23]	125.7 [23]
$CH_2O* + H* \leftrightarrow CH_2* + OH*$	163.7 [23]	154.1 [23]
$CO* + * \leftrightarrow C* + O*$	237.4 [23]	111.8 [23]
$CO* + 2H* \leftrightarrow CH* + OH* + *$	221.4 [23]	146.1 [23]
$2CO* \leftrightarrow CO_2* + C*$	339.6 [24]	109.0 [24]
$C* + H* \leftrightarrow CH* + *$	69.2 [23]	154.1 [23]
$CH* + H* \leftrightarrow CH_2* + *$	68.2 [23]	61.9 [23]
$CH_2* + H* \leftrightarrow CH_3* + *$	71.4 [23]	105.6 [23]
$CH_3* + H* \rightarrow CH_4 + 2*$	137.4 [23]	178.7 [23]
$O* + H* \leftrightarrow OH* + *$	137.9 [23]	116.0 [23]
$OH* + H* \leftrightarrow H_2O* + *$	137.9 [23]	99.9 [23]
$H* + * \leftrightarrow * + H*$	13.0 [22]	13.0 [22]
$CO* + * \leftrightarrow * + CO*$	10.0 [22]	10.0 [22]
$O* + * \leftrightarrow * + O*$	48.0 [22]	48.0 [22]
$OH* + * \leftrightarrow * + OH*$	21.0 [22]	21.0 [22]

Table 1. Elementary processes intervening in the $H_2 + CO_2$ and related activation energies (with the source reference in the rhs) for the forward and reverse process.

It is worth noticing here that the kinetic system of equations does not include at present pure gas phase reactions because, at the energetic conditions considered for our runs, they are not competitive with those occurring through adsorption on the surface of the catalyzer. The second important point to make is that, as common to many kinetic simulation packages, the rate coefficients k_p of the intervening elementary processes p are expressed in an Arrhenius like form (ie. as the product of a pre-exponential factor (A) and an exponential term (X)). The two terms refer to an intermediate molecular geometry of the system assumed to be a transition state separating reactants from products along a properly chosen reaction coordinate. Moreover, once crossed, the transition state is assumed not to be recrossed back. Empirical corrections to this formulation are sometimes introduced by mitigating the no-recrossing condition and by introducing a steric factor accounting for the different efficiency of the process as the attack angle is varied. The exponential term is usually expressed as $X = e^{-E_p/k_B T}$, where k_B is the usual Boltzmann constant and T is the temperature of the system. E_p is a parameter quantifying the energetic barrier to reaction associated with the PES of the related elementary process p (for the direct or forward "f" and the reverse or backward "b") ie. 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 the one associated with the original asymptote of the process. The values of E_p collected from the quoted references for both forward and reverse processes are reported in the central left and the central right columns, respectively, of Table 1. In the transition state approach adopted in our investigation, for entirely surface processes the pre-exponential factor can be formulated as $A = k_B T/h$ (where h is the Plank constant) while for adsorption processes, reaction rate (r_i) can be obtained from the well-known Hertz-Knudsen equation:

$$r_i = \frac{p_i A_{site}}{\sqrt{2\pi m_i k_B T}},$$

where p_i is the i species' partial pressure, A_{site} the surface area of adsorption site and m_i the mass of species i.

On this ground, we implemented a version of ZACROS [25, 26], a kinetic Monte Carlo (kMC) [27, 28] software package written in Fortran 2003, for simulating the kinetic behaviour of the H_2 + CO_2 system. ZACROS properly deals with molecular phenomena on catalytic surfaces [29] 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. The rates of these elementary processes are expected to be computed in an *ab initio* fashion so as to enable the prediction of catalytic performances (such as activity and selectivity) from first principles. 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.

4 The simulation and its results

In spite of being the Sabatier reaction a well established textbook example, the mechanism of the Ni-catalyzed CO_2 methanation is still not fully understood as we shall discuss later in this section. The already mentioned preliminary measurements on PROGEO performed by A. Capriccioli suggest that the production of CH_4 with a H_2/CO_2 ratio of 5:1 (hydrogen excess) is effective in producing CH_4 with a good yield. Two main mechanisms have been proposed: schema (A) considers the reaction happening through adsorbed CO as intermediate [30, 31], while schema (B) considers a direct hydrogenation of adsorbed CO_2 [32, 33]. Furthermore, even for the subsequent steps of the first schema (the CO hydrogenation to methane) there is no consensus on the further steps. One hypothesis maintains that reaction evolves towards a CO dissociation to C + O, another considers the CO to be directly hydrogenated while a third one proposed by Martin et al. [34] considers the mechanisms mainly occurs through the disproportionation of CO, being, in all three cases, the proposed reaction the rate limiting one.

The kinetic Monte Carlo (kMC) simulations performed by us include the four aforementioned schemas as illustrated in Table 1. By using the activation energy values given in the table and the appropriate preexponential factor, the time evolution of the system components was computed at the desired conditions of temperature, pressure and initial gas phase molar fractions.

As a first step, an optimization of the most important parameters of the kMC simulation has been performed. When taking original reaction rates, simulation times are really small. This happens because the kinetic Monte Carlo timestep ($\mathit{\Delta} t$) is taken as

$$\mathit{\Delta} t = \frac{1}{\sum_{i=1}^{n} \sum_{j=1}^{k} r_{ij}},$$

where r_{ij} is the ith reaction on the jth site, n is the total number of considered steps and k the number of sites. Since diffusion rates are far larger than reactive ones, the system spends most of the time simulating the first ones. In order to accelerate the convergence of the calculations, prexponential factors for diffusive processes were multiplied by a α scaling factor ($\in$ (0,1]). When this scaling factor is applied a huge increase in timestep is obtained, enabling to simulate longer times. It is always important to take care that no change on the final results would occur when applying this scaling factor. The final adopted values of α are given in Table 2 which led to six orders of magnitude increase in the simulated time.

Process	**original preexponential factor**	**α coefficient applied**
$H^* + * \leftrightarrow * + H^*$	$2.027 \cdot 10^{13}$	10^{-4}
$CO^* + * \leftrightarrow * + CO^*$	$2.027 \cdot 10^{13}$	10^{-5}
$O^* + * \leftrightarrow * + O^*$	$2.027 \cdot 10^{13}$	10^{-2}
$OH^* + * \leftrightarrow * + OH^*$	$2.027 \cdot 10^{13}$	10^{-3}

Table 2. Elementary processes which optimized scaling factor α was applied.

Another parameter that was also optimized in the simulation is the size of the grid (given as the number of copies of the unit cell in two dimensions). It is to be clarified that in our case the unit cell used is not the primitive but one containing two sites. In this case too, a compromise between the length of the simulation time and the convergence of the results was to be found. A value of 25x25 unit cells was found to reproduce same results as larger lattices while significantly reducing computation time.

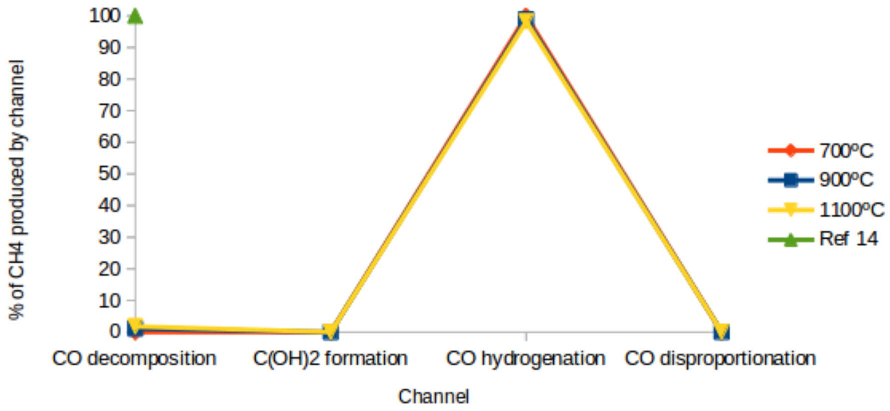

Fig. 1. Percent of formation of CH_4 from the different candidate rate determining steps (reaction mechanism). Green value is not quantitative but only to indicate which is the rate limiting step proposed.

Using the optimized parameters several runs were performed by varying the temperature (T=300, 500, 600, 700, 800, 900, 1000 and 1100°C) to show which mechanism was the one that occurred the most. The rate limiting steps of each one were the CO decomposition (CO* + * ↔ C* + O*), the $C(OH)_2$ formation (CO_2* + 2H* ↔ $C(OH)_2$* + 2*), the CO hydrogenation (CO* + 2H* ↔ CH* + OH* + *) and the CO disproportionation (2CO* ↔ CO_2* + C*). Computed results show that while at 300 and 500 °C, no CH_4 is formed, from 600 to 1100 methane is indeed produced and, as shown in Fig., 1 the largest fraction of produced CH_4 (well above 90%) is obtained from mechanism A (the hydrogenation of the adsorbed CO concretely through the process CO* + 2H* ↔ CH* + OH* + *).

Accordingly, the CO decomposition plays always a residual (even more marginal at low temperatures) role. This finding is in contrast with the dominance of mechanism B proposed by the authors of ref [23] that postulates a CO decomposition into C + O on the ground of some *ab initio* electronic structure considerations (see the green triangle shown on the lhs of Fig. 1) without resorting into a true kinetic study.

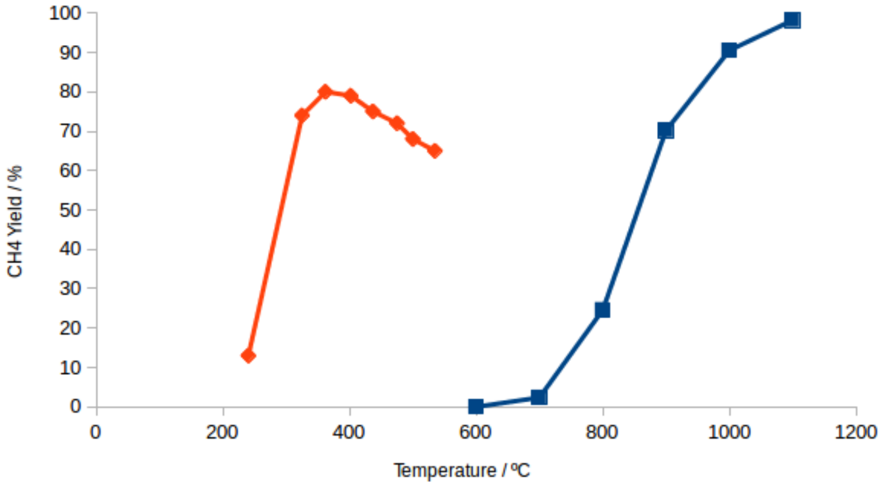

Fig. 2. Plot of the yield of CH_4 as a percent of the reactant CO_2.

The analysis of the computed CH_4 yield at a pressure of 10 atm and a H_2/CO_2 ratio of 5:1 as a function of T (see Fig. 2) exhibits a threshold at about 700°C. The yield grows to about 70% at 900°C and reaches almost 100% at 1100°C. This behavior is in line with the fact that the rate determining step of the CH_4 production was found in our calculations to be the hydrogenation of CO* that has a higher energy barrier than that of the CO production but also a higher pre-exponential factor leading to higher production at high temperature. As is apparent from the Figure there is a clear difference between the measured and the computed threshold temperature [35], possibly due to the fact that we were simulating only Ni(111) surface instead of the whole catalyst, which is far more complex. As a matter of fact, the computed threshold temperature is 600°C higher than that of the experiment and the computed rate of increase of the yield as a function of T is one half of that of the experiment. However, being our simulation the first attempt to obtain a computational estimate of the yield of the Ni catalyzed process of PROGEO, it is not suprprising that though not quantitative the agreement between the experiment and the simulation is satisfactory.

5 Conclusions and possible developments

In this paper we discuss the problems met when implementing a simulation of the PROGEO methanator.

The general qualitative agreement of the simulation with the experimental results shows that not only the problem is a suitable problem to investigate and improve on the proposed European Research infrastructure but it already confirms that mechanisms suggested on the pure ground of *ab initio* electronic structure calculations can be completely wrong. On the contrary even simplified (assuming Arrhenius like formulations of the rate coefficients) calculations lead to results qualitatively agreeing with measurements performed on an experimental apparatus. On the computational side, however, the quantitative differences between computed and measured quantities confirm that there is need for improvement obtainable for a more complex collaborative RI approach. In a RI approach, in fact, the expected improvements are provided not only from the possibility of getting accurate *ab initio* data (thanks to the better availability of high level HPC compute resources) but also from the possibility of better handling first raw data and then related metadata, of combining complementary expertise, of picking up more appropriate codes.

Moreover, the discussion of the results obtained clearly indicates the need for further improvements in the:

- evaluation of the performance of the simulation under different conditions like different pressure or gas phase reactive molar fractions;
- improvement of the chemical mechanisms with the incorporation into the formulation of the rate coefficients corrective terms associated with the partition functions of reactants and transition states, tunneling effects, sticking coefficients, etc.;
- investigation of the possibility of obtaining the evaluation of the rate coefficients from accurate dynamical calculations;
- performing a sensitivity analysis to evaluate the effect of different catalysts.
- better integration of conditions with output statistical analysis and further graphical tools supporting a better understanding and a multimedia dissemination of the results.

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