THE DEVELOPMENT LINES OF PROGEO

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PREAMBLE

The ICSA (Innovative Computational Science Applications) Association has started several years ago in collaboration with some scientific Institutions (the Universities of Roma Tor Vergata, Roma 3 and Perugia, the CNR Institute on Membrane Technology ITM of Rende (CS), and ENEA), with the technological support of a cluster of three companies (R.P.C srl, Master-UP srl, RDpower srl) and the financial and technical aid of the PLC-System srl. The PROGEO project has produced the **30 kW** experimental industrial prototype apparatus (named PROGEO 30 kW).

To the end of enhancing research activities and innovation from the evolution of PROGEO 30 kW it has been agreed to transfer the prototype apparatus from the PLC System, where it has been mounted, to the University of Perugia within the frame of the **ITN-EJD-642294 TCCM** (Theoretical Chemistry and Computational Modelling) European project under the joint supervision of the Department of Chemistry, Biology and Biotechnology (Prof. A. Laganà) and the Department of Civil and Environmental Engineering of Perugia (Prof. S. Falcinelli).

PROGEO 30 kW (30 kW peak value; 20 kW nominal value) has a nominal carbon neutral (from CO_2 reduction by electrolytic H_2) methane production varying from 1 to 1.5 Nm^3/h as described in the PCT: WO 2012/1900581 A1 with the title: "Unit for the accumulation of electrical energy via production of methane". The prototype can recover the heat of the outlet gas from the reactor by heating the inlet gas, using intrinsically passive safety elements and making flexible use of the heat generated during methanation reaction through an innovative interface with variable thermal conductivity.

Current Academic research for PROGEO is focused on the rationalization of the methanation process carried out using prototype reactors (like the already mentioned PROGEO 30 presently located at the university of Perugia. At the same time industrial developments of PROGEO will focus on miniaturization of its components in order to improve its commercialization for low-power use and its modularity for high power use.

THE COMPUTATIONAL TOOLS OF MASTER-UP: the University of Perugia Academic Spinoff

MASTER-UP SRL (Molecular Applications to Science, Technology, E-learning and Research - University of Perugia) is an Academic spinoff of the University of Perugia. It was founded in 2004 by a full professor, a researcher, a technical staff and 4 contract researchers in order to develop know how and Hardware/Software support to the accurate realistic study of molecular and materials structures and processes and to related innovative technologies. Accordingly, two mainstreams of activities have been developed

1. A PRIORI MOLECULAR SIMULATIONS: studies concerned with the in silico assemblage and modification of molecular and nano-structures (of high impact in the design of new materials, drugs, food, textiles, etc.) as well as with the in silico modelling and control of molecular dynamics and kinetics (of high impact in energetics, life science, plasma physics etc). The focus of this type of activities is on environmental, technological and industrial innovation obtainable from research transfer into marketable products.

2 KNOWLEDGE PRODUCTION AND MANAGEMENT ON THE NET: development and implementation on concurrent platforms of middleware, environments, tools and applications for problem solving and (meter and nano scale) virtual reality as a support for research and technology transfer from accademic research to market in services, industry and education.

Accordingly the MASTER-UP activities aimed at supporting the design and development of PROGEO are:

- the use and development of an accurate multiscale simulator implemented on distributed platforms. Such simulator is GEMS (the Grid Empowered Molecular Simulator gathering in a common workflow programs devoted to the calculation of the electronic structure of molecular aggregates, the integration of motion of atomic and molecular system, the average over unobservable parameters to assemble virtual experimental signals in beam experiments).

- the management of multicomputer clusters connected in distributed cloud and grid platforms. A typical esample is GEMINI (the combination of a cluster rack of 50 four core elements and a cluster rack of 16 dual core elements) acting as local CEs, SEs and front end of the European Grid Initiative (EGI) and of the Italian Grid Initiative (IGI) devoted to the computational activities of the Virtual Organization (VO) COMPCHEM providing the Chemistry community with annual cpu hours of the order of several millions. The extension of the platform with a mass storage of several TBs and a virtual reality laboratory is being planned.

- the design of educational environments and tools. A typical example is the National Test Center of Perugia for EChemTest® (a European service infrastructure for self assessment electronic tests sessions in Chemistry knowledge developed by the ECTN (European Chemistry Thematic Network) Association) of which MASTER-UP takes care of developing a commercial line.

- research and innovation transfer in industrial activities. Typical examples is PROGEO (a research project aimed at developing technologies to be employed to realize an industrial apparatus allowing the storage of excess alternative energy as chemicals).

- design and implementation of software for innovative computing architectures. Typical examples are GriF (a tool for evaluating Quality of Users and Quality of Services for virtual communities), GPU utilities (software tools for the exploitation of multi treading processing units.

- editorial activities in the field of academic and specialistic lecture notes, the organization of training schools and workshops, the design and development of learning objects and e-learning material

- participation to science and innovation national and international projects.

THE MODELING OF THE (SOLID STATE) CATALYZED METHANATION REACTION

All the above mentioned activities have been exploited to the end of pursuing a high efficiency of PROGEO as well as the rationalization of the mechanisms of the CO_2 reaction.
The chemical reaction occurring inside the experimental prototype apparatus of PROGEO has been assembled at the industrial premise of the PLC System. The apparatus assembled is based on the

(solid state) catalysed reduction of CO_2 by H_2 (commonly called Paul Sabatier reaction) whose stoichiometrically balanced form reads:

$$CO_2 + 4H_2 + * \rightarrow CH_4 + 2H_2O + *.$$

The reaction is catalyzed by Nickel at high temperature (300-400 °C) and high pressure to produce methane and water (a more efficient catalyser is ruthenium on alumina). Figure 1 shows typical yields obtained from preliminary runs of PROGEO.

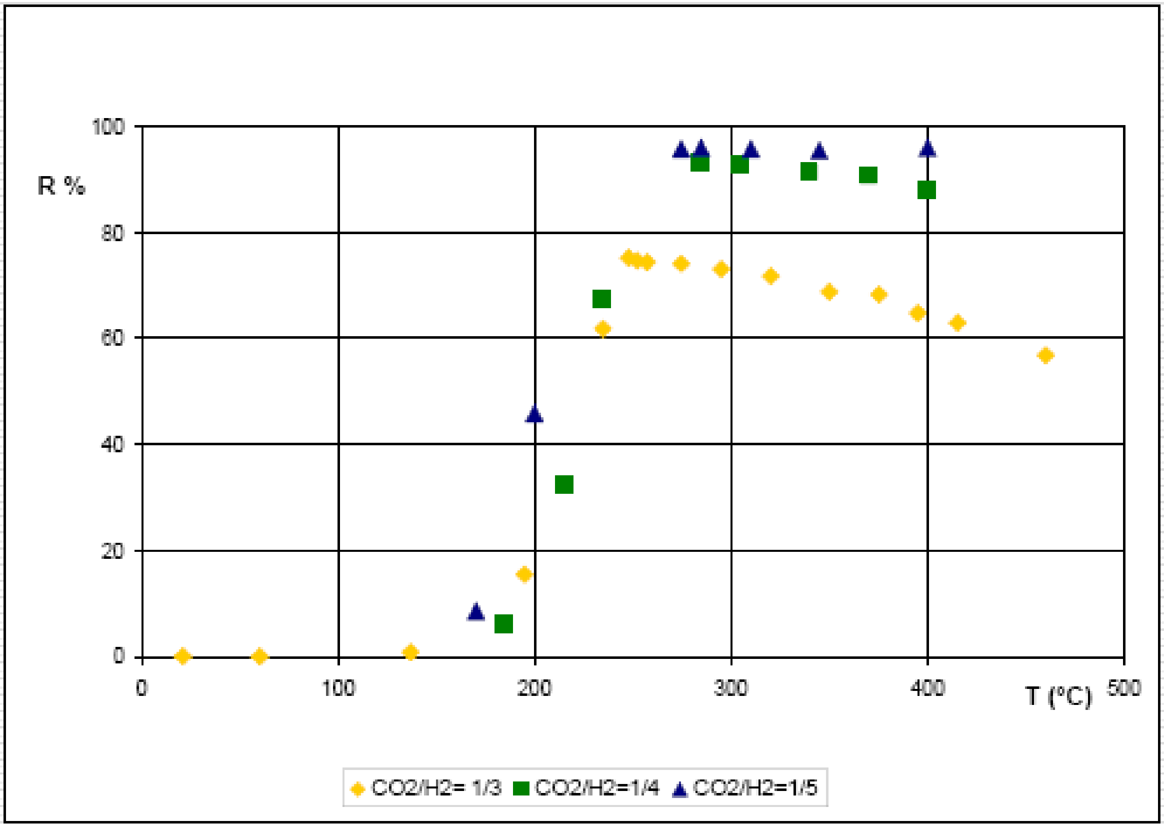


FIG. 1 – CH_4 per cent methane yield plotted as a function of T at different CO_2/H_2 ratios

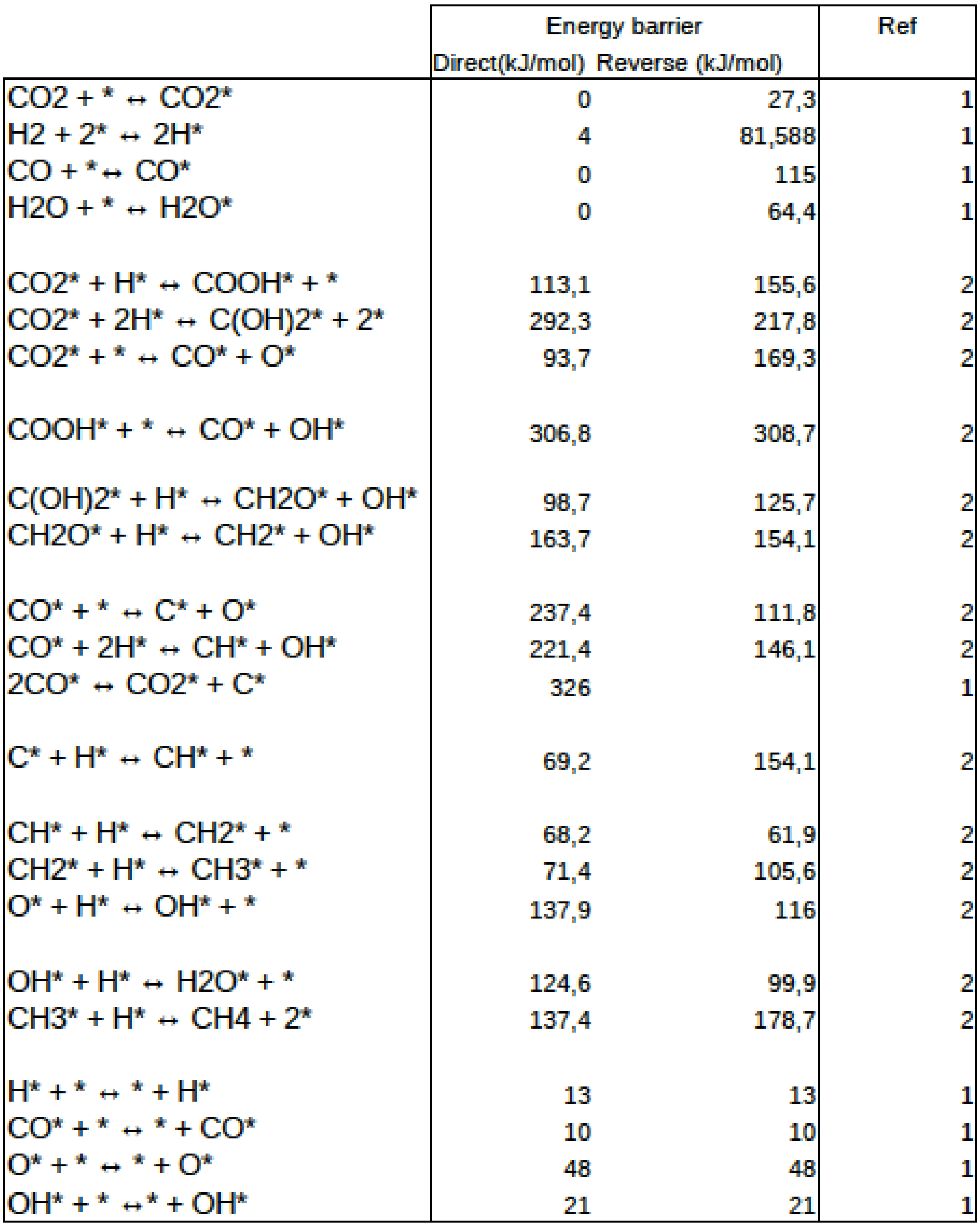
The modeling of the process is going through the following steps:

1 decompose the Paul Sabatier reaction into its elementary components

2 evaluate the rate coefficients of the elementary components

3 integrate the kinetic equations coupling the concentrations of the intervening species in order to evaluate the yields

The initial step (1) of the modeling process, consisting in the decomposition of the Paul Sabatier reaction into elementary components, has been already completed. As is apparent from TABLE 1, shown below, there are several processes potentially concurring to the Paul Sabatier reaction. They all occur via the adsorption of the gas phase on the catalyzer. Related elementary processes are listed in TABLE 1. Rate coefficients of the listed processes can be evaluated using a simplified transition state theory formula $k=A\exp(-E_p/k_BT)$ with A being k_BT/h, p the label for either the direct or the reverse process and E_p the activation energy quoted in the Table for the related process



	Energy barrier		Ref
	Direct(kJ/mol)	Reverse (kJ/mol)	
CO2 + * ↔ CO2*	0	27,3	1
H2 + 2* ↔ 2H*	4	81,588	1
CO + *↔ CO*	0	115	1
H2O + * ↔ H2O*	0	64,4	1
CO2* + H* ↔ COOH* + *	113,1	155,6	2
CO2* + 2H* ↔ C(OH)2* + 2*	292,3	217,8	2
CO2* + * ↔ CO* + O*	93,7	169,3	2
COOH* + * ↔ CO* + OH*	306,8	308,7	2
C(OH)2* + H* ↔ CH2O* + OH*	98,7	125,7	2
CH2O* + H* ↔ CH2* + OH*	163,7	154,1	2
CO* + * ↔ C* + O*	237,4	111,8	2
CO* + 2H* ↔ CH* + OH*	221,4	146,1	2
2CO* ↔ CO2* + C*	326		1
C* + H* ↔ CH* + *	69,2	154,1	2
CH* + H* ↔ CH2* + *	68,2	61,9	2
CH2* + H* ↔ CH3* + *	71,4	105,6	2
O* + H* ↔ OH* + *	137,9	116	2
OH* + H* ↔ H2O* + *	124,6	99,9	2
CH3* + H* ↔ CH4 + 2*	137,4	178,7	2
H* + * ↔ * + H*	13	13	1
CO* + * ↔ * + CO*	10	10	1
O* + * ↔ * + O*	48	48	1
OH* + * ↔* + OH*	21	21	1

TABLE 1 – LIST OF THE ELEMENTARY PROCESSES CONSIDERED FOR THE Ni CATALYZED (the catalyst is represented by *) REDUCTION OF CO_2 TO CH_4 **(**Ref 1 J. Phys. Chem. C, Vol. 113, No. 12, 2009; Ref 2 J. Ren et al. / Applied Surface Science 351 (2015) 504–516)

The rate coefficients of the intervening elementary processes are usually expressed in terms of the Transition State theory (TS) as the product of a pre-exponential factor (let us call it as A and an exponential term. The two terms refer to an intermediate molecular geometry of the system associated with the TS (ie the one separating reactants from products along a properly chosen coordinate (reaction coordinate) that excludes the possibility for the molecular system to regress back into the reactant region once entered the product one).

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 in energy between the stationary point of the potential Minimum Energy Path (MEP) at the transition state and the initial 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 Plank constant.

A better approximation formulates the pre-exponential factor differently depending on whether the processes involve the gas phase (ie. adsorption and desorption steps) from those occurring entirely on the surface. In this case the method takes into account the molecularity of the process when it involves only ????? adsorbed species.

For the adsorption the pre-exponential term takes the form:

$$A = \left(\frac{k_BT}{h}\right)\left(\frac{RT}{P_0}\right){N^0}_{sites}C_T,$$

where R is the gas constant, P_0 the standard pressure, C_T the concentration of binding sites, and N^0 the number of binding sites per adsorbate. Whereas in the case of fully adsorbed processes the pre-exponential term takes the form:

$$A = \left(\frac{k_BT}{h}\right)\left(\frac{{{N^0}_{sites}}^{R_{tot}-1}}{{C_T}^{R_{ads}-1}}\right)$$

where R_{tot} is the total number of reactants participating in reaction (including vacant sites) and R_{ads} is the total number of adsorbate reactants (not including vacant sites).

An even 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):

$$A = \left(\frac{k_BT}{h}\right)\left(\frac{{{N^0}_{sites}}^{R_{tot}-1}}{{C_T}^{R_{ads}-1}}\right)\left(\frac{Q^{TS}({Q'}_{slab})^{R_{tot}-1}}{\prod_{r=1}^{R_{tot}} Q_r}\right)$$

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 traslations are frustrated and therefore become 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 specie X, and k refers to the vibrational normal modes.

A comparison of the methods illustrated above is given below

IMPROVING THE MODELING FOR INNOVATING THE METHANATION PROCESS

A first improvement of the modeling can be obtained by better formulating the Rate coefficients. In fact, even within a pure transition state approach, both the pre-exponential coefficient A and of the activation energy E_p can be more rigorously formulated and evaluated using statistical considerations and quantum chemistry calculations of the transition state electronic structure. Using such data one can run a Monte Carlo simulation and obtain the yields of the simulated complex process.

A second improvement of the modeling can be obtained by merging the treatment with the Grid Empowered Molecular Simulator (GEMS) that replaces transition state treatments with quantum and classical (or quantum-classical) dynamical calculations of the cross section and evaluating the rate coefficients by integrating over collision energy and averaging over the proper distribution of internal energy. Dynamical calculations themselves are based on accurate ab initio calculations of the overall process potential energy channel. In this way one is able to leverage on rigorous theoretical and computational means allowing to make the make the modeling predictive.

A third more important improvement is to consider the simulator for extending its predictive capabilities to model elementary processes taking place under proper conditions exclusively in the gas phase in order to avoid problems arising from the poisoning of the catalyzer. By exploiting the well established expertise of several European Universities and Research Centers in detailed studies of the properties of gas phase systems (beam-beam, beam gas, spectroscopy, plasma, etc studies) alternative mechanisms for methanation can be worked out.