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Networked computing for ab initio modeling the chemical storage of alternative energy: Third term report (March-May 2016)

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Abstract

During the last term, substantial progress has been made in better understanding the Ni-catalyzed Sabatier reaction. Kinetic Monte Carlo simulations have been performed using data listed in the report of the previous term. The simulations have been repeated at different values of temperature to the end of both characterizing its threshold value and determining its interval of maximum yield. A sensitivity analysis study has also been performed in order to figure out the rate determining steps of the methane production mechanism. During the term progress has been made also in mastering the Quantum-classical method illustrated in the previous report and in applying it to some key diatom-diatom processes. In particular the program has been used to compare quantum with quantum-classical estimates of the state specific probabilities of the OH+H_2 reaction computed on a new potential energy surface and to evaluate as well the state-to-state vibrational inelastic transition probabilities of the reactant channel. Finally, in order to cope with the associated heavy computational burden of the calculations, the code has been parallelized using the Shared Memory paradigm. Compute time measurements lead to a speedup of 3.9 when using 4 cores. In order to widen my computational competences I attended also a school of the ITN-TCCM Consortium on the ADF software package.

Report

1) Kinetic Monte Carlo (kMC) study of the Sabatier reaction

In the report of the previous term the basics of the kMC method were outlined and the values of the Arrhenius formulation of the reactivity parameters (mainly the energy barriers of the processes involved in our simulations) were analysed [1]. The simulations were aimed at determining the optimal operating conditions of PROGEO (at present they are a pressure of up to 10 atmospere and an H_2/CO_2 ratio of 5:1). Two main mechanisms have been proposed in the literature for the Sabatier process:

- schema (A) the reaction occurs via the adsorption of CO on the Ni catalyser as reaction intermediate [2, 3],
- schema (B) a direct hydrogenation of the adsorbed CO_2 occurs [4, 5].

Furthermore, for schema (A) even for the steps following the CO adsorption (its hydrogenation to methane) there is no agreement. An hypothesis assumes that reaction evolves first towards a dissociation of the adsorbed CO to C + O while another hypothesis assumes the adsorbed CO to be directly hydrogenated. A third hypothesis assumes that the mechanism proceeds through the disproportionation of the adsorbed CO. However, in all three cases, the proposed reaction is the rate limiting step. The goal of our investigation has been thus to figure out, through simulations, which is the most likely rate determining step of the methanation mechanism, and how to reproduce both the temperature dependence of the process and its threshold value.

In order to enhance the computational efficiency of the simulations we optimized some of the most important parameters of the procedure (as discussed in the communication delivered at the ICCSA (International Conference of Computational Science Applications) of Beijing [7]).

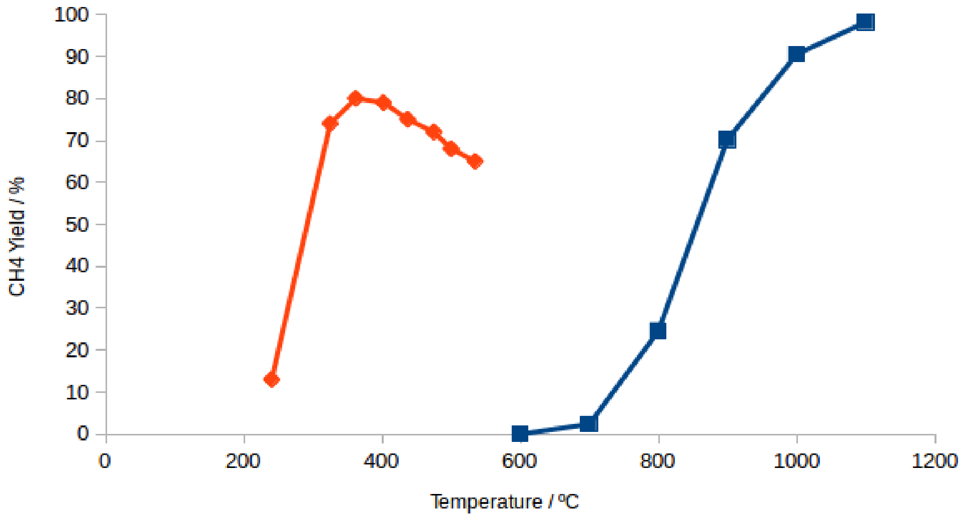

Fig. 1. Plot of the measured (red) and computed (blue) yield of CH_4 as a percentage of the reactant CO_2 [7].

The simulations (see blue line of Fig, 1) give a threshold temperature of about 600^{o}C[8] (about 400^{o}C higher than that of the experiment (red line)) and an increaseof the yield with temperature is less sharp than the measured one (although it reaches 100% just above 1000°C while the experiment reaches a maximum of about 80% just below at 400°C). Among the limits of the simulations, however, it has to be noted that the experimental catalyser is not Ni(111), as used in the calculations, but a special Ni-based solid with a far more complex structure.

Despite the just mentioned quantitative discrepancies the indications obtained by the simulations provide interesting insights on the methanation mechanism. They in fact single out that, as shown in Fig. 2, the CO hydrogenation is the rate determining step, and the reaction evolves according the following sequence of steps: CO_2* (the asterisk (*) indicates an adsorbed species) is first dissociated into CO* + O*and the obtained CO* is hydrogenated by 2H* to form CH* and OH*. Then CH* is further hydrogenated in 3 subsequent steps by H* to become CH_4, while OH* also gets hydrogenated to water by H*. This finding is in contrast with the dominance of mechanism B proposed by the authors of ref. [9] 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 upper corner of Fig. 2) without resorting into a true kinetic study. Another observed effect is the large amount of COOH* produced, which does not

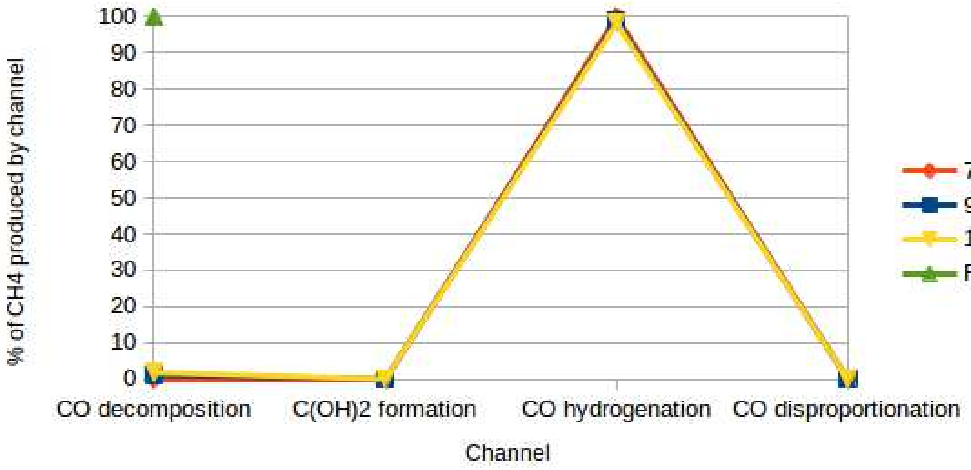

Fig. 2. Percent of formation of CH_4 from the different candidate rate-determining steps. The green triangle in the upper left corner of the figure indicates the value of the rate limiting step proposed in ref. [9].

evolve to CH_4 and remains adsorbed on the catalyser surface leading to a poisoning of the catalyst. This fact encouraged us to perform a sensitivity analysis by varying the energy barriers of some key steps of the whole process. In order to evaluate the role played by COOH* (ie. the absorption of COOH* on the cathalyser) in one case we raised the energy barrier of its formation while in another case we decreased the energy barrier of its decomposition. We also raised the energy barrier of the rate determining step to evaluate the effect it has on the methane production.

Fig. 3 shows the production of CH_4 molecules with time as a result of the above mentioned changes. The figure tells us that both the inhibition of the COOH* formation (red) and the enhancement of its decomposition (green) strongly favour the CH_4 formation with respect tothe original simulation using the energy available from the literature with no modification (cyan). On the contrary, the inhibition of the CO* hydrogenation (blue) completely prevents the CH_4 production, further proving, so far, that this is the rate limiting step of the whole process.

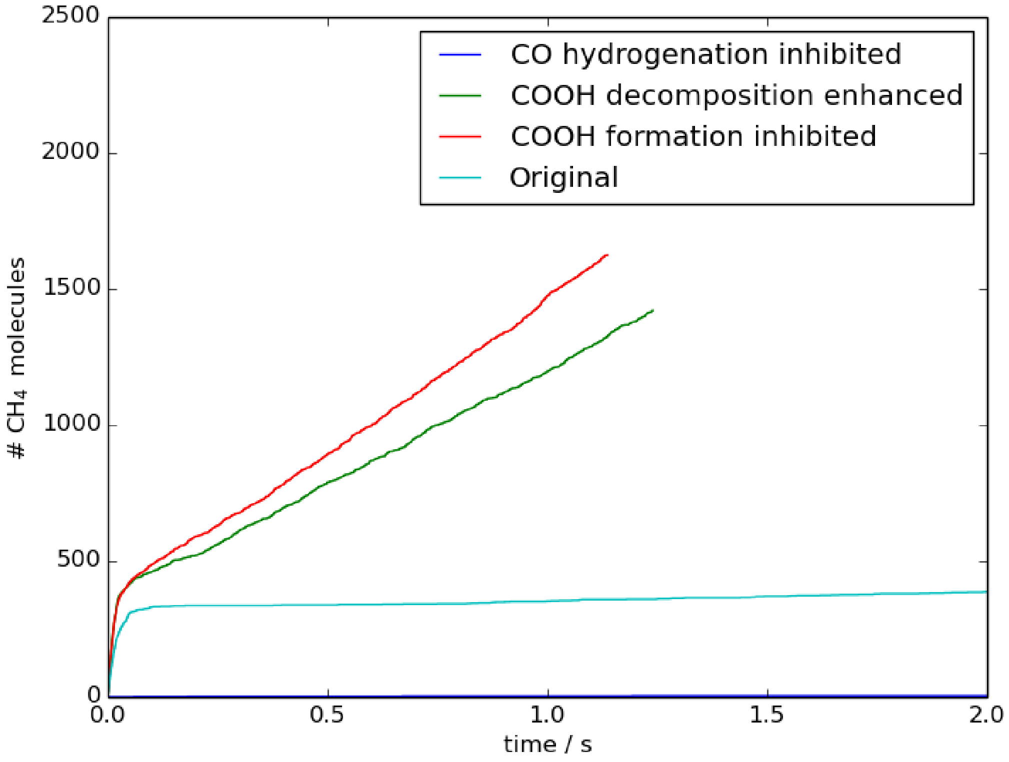

Fig. 3. Sensitivity analysis of CH_4 formation upon time: the variation of the CH_4 yield when changing the most important energy barriers.

2) Quantum-classical study of the OH + H_2 → H_2O + H reaction

In the 1st term report[8] we gave an overview of the theoretical basis of the quantum-classical methodology [10]. Since then several simulations, including those for the hydrogen cyanide benchformation reaction CN + H_2 → HCN + H and those for the hydroxyl combustion OH + H_2 → H_2O + H, were performed. Calculations for the former process, were run in order to gain familiarity with the methodology and the code itself. For it we can quote that the goal of reproducing the already published results was, indeed achieved. For the second process the main goal was to check our quantum-classical estimates of the state specific reactive probabilities against the published exact quantum values of Zhang et al. [11, 12] and to evaluate as well the state-to-state vibrational inelastic (non reactive) transition probabilities. The comparison of our quantum-classical results (red line) and the Zhang quantum ones (green line) is given in Fig. 4. The figure shows that there is indeed an excellent agreement between our results and the quantum ones (discrepancy is less than a few percents). A detailed

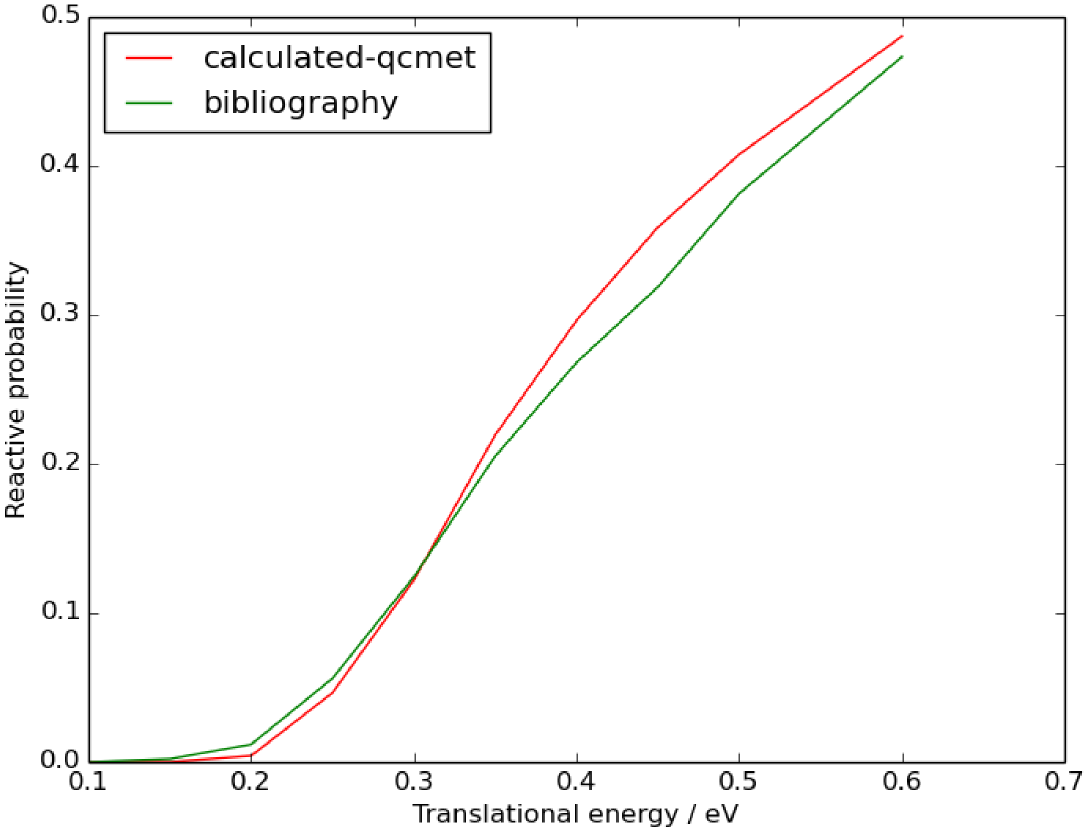

Fig. 4. Comparison of our state specific quantum-classical estimates of the reactive probabilities (qcmet, red line) and the quantum results of Zhang et al. [12] (green line).

analysis of the state-to-state vibrational inelastic (non reactive) transition probabilities is at present being carried out and its outcomes will be presented in the next report.

3) Parallelization of QCMET using the Shared-Memory paradigm

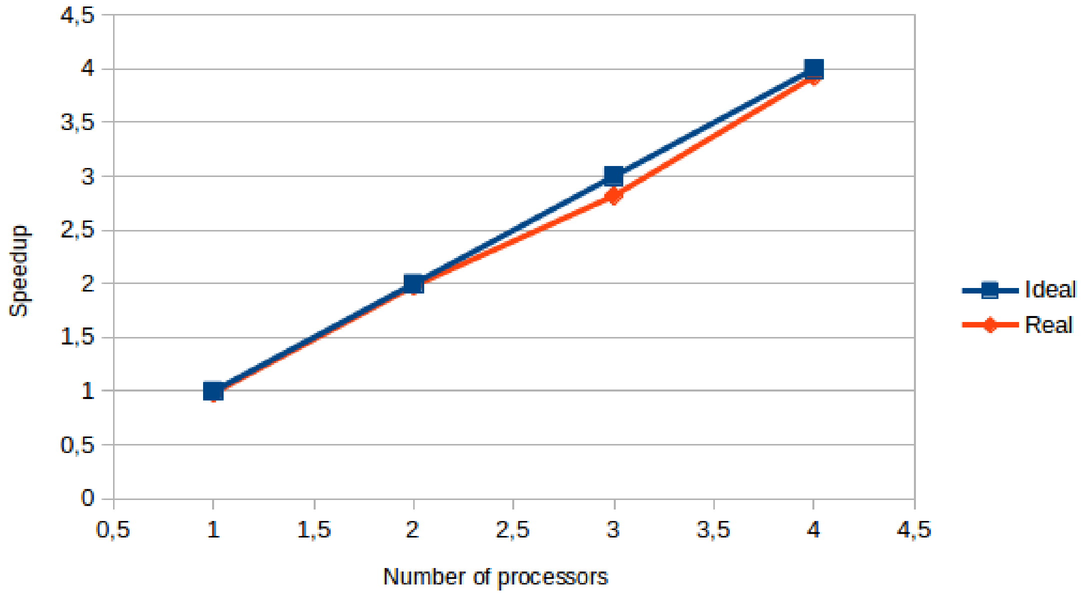

Fig. 5. Speedup of the parallelized code up to 4 cores (red line) compared with the ideal value of 100%

In order to exploit the excellent agreement between the quantum-classical results and the quantum ones for carrying out kinetics simulations of complex gas phase systems (like those necessary for the accurate modelling of aerothermodynamics, laser and plasma physics) we have parallelized the code to the end of enabling massive calculations of related detailed cross sections and rate coefficients at high energies and temperatures, for which quantum calculations are practically unfeasible. As a first approach we decided to try a Shared memory paradigm, using the OpenMP standard. To do so, a severe revision of the code was needed, and a in dept restructuring was carried out to the end of changing the old-fashioned structure of the code according to the new standards recommended by the Programming community (from Fortran 77 to Fortran 90 for example). This has involved the analysis of variable types, the rearrangement of subroutines and output calls, the management of vectors and matrices, etc. The speedup achieved when using the parallelized code up to 4 processors is plotted in Fig. 5..

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