

Enclosure 1b. Category 1 Application form 2015 – English version

APPLICATIONS ARE PREFERABLY DRAWN UP IN ENGLISH. AN ENGLISH TRANSLATION HAS TO BE ENCLOSED WITH APPLICATIONS SUBMITTED IN DUTCH.

The application form is available in Dutch on the website <https://vscentrum.be/>.

Title of the application:

Dynamical first principle benchmark study on alkene methylation in H-ZSM-5

Name and first name of the applicant:

De Wispelaere Kristof

Institution:

Ghent University

Research group / department:

Center for Molecular Modeling

Title / position:

Dr. ir. / ERC postdoctoral researcher

E-mail address:

Kristof.DeWispelaere@UGent.be

Total computing time that is needed, in node days:

1400

Total disk storage that is applied for (in GiB):

125 GB scratch space – 200 GB long-term storage (provided by UGent)

1. Title of the research project (with IWETO or FRIS link if available) within the framework of which computing time is applied for:

European Union's Horizon 2020 research and innovation programme (consolidator ERC grant agreement No 647755 – DYNPOR (2015-2020))

2. Describe your research project in short. Explicitly mention the scientific questions that you are planning to address and the overall scientific goals of the project. (max. 1 A4 in Arial 12):

Alkene methylation reactions are relevant reaction steps in the framework of the conversion of methanol to hydrocarbons (MTH) in zeolitic materials. A couple of years ago accurate experimental kinetic data for alkene methylation in H-ZSM-5 became available [1] and later on Van Speybroeck et al. [2] and Sauer and co-workers [3] succeeded to predict the kinetics of these alkene methylation reactions with near chemical accuracy with a static approach on extended finite cluster models.

Recently, ab initio molecular dynamics (AIMD) techniques entered in the field of zeolite-catalyzed reactions. MD studies revealed that temperature effects, zeolitic framework flexibility and the presence of additional guest molecules around the reactants may significantly impact the mechanism and kinetics of zeolite-catalyzed reactions. Therefore, we want to perform an extensive benchmark study to test the accuracy of free energies and reaction kinetics predicted by a range of MD-based techniques.

A systematic series of alkenes will be studied, being ethene, propene, 1-butene, 2-cis-butene, 2-trans-butene and isobutene as depicted in Figure 1. For the co-adsorbed systems of methanol and each of the alkenes in H-ZSM-5 regular MD, metadynamics (MTD) and constrained dynamics (CMD) will be performed by applying a Density Functional Theory (DFT) based scheme. Hereby both the concerted reaction mechanism will be adopted in first instance.[4] After analysis of the free energy surface (FES) from the MTD simulations or after performing thermodynamic integration with the information obtained after the CMD simulations free energy barriers and kinetic coefficients for the methylation reactions can be deduced. Additionally, the effect of applying Becke Johnson (BJ) damping in the DFT-D3 correction scheme for dispersion will be assessed.

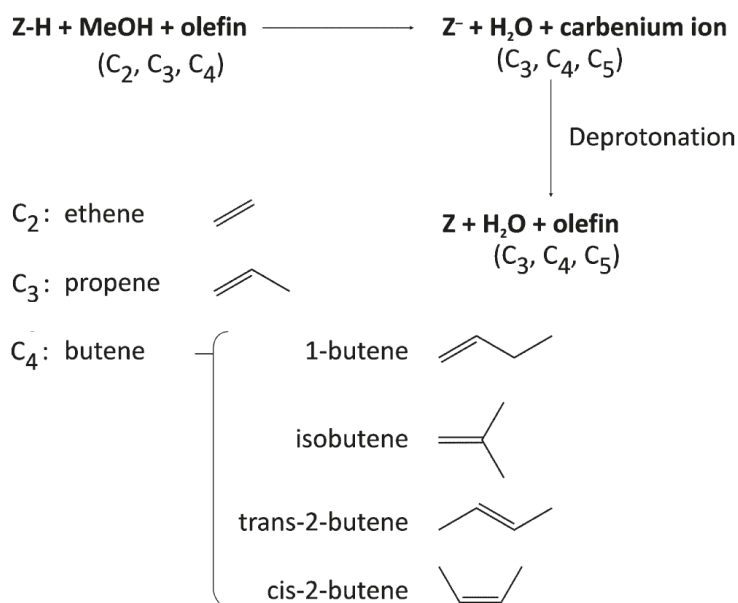


Figure 1. Schematic representation of the studied alkene methylation reactions in the benchmark study. Taken from ref [2].

With this thorough benchmark study we will be able to demonstrate the strength and added value of a dynamical approach when modeling zeolite-catalyzed reactions under realistic reaction conditions. A paper forthcoming from this study will undoubtedly have a very high impact.

[1]Svelle, S.; Ronning, P. A.; Kolboe, S. J. *Catal.* 2004, 224, 115.; Svelle, S.; Ronning, P. O.; Olsbye, U.; Kolboe, S. J. *Catal.* 2005, 234, 385.

[2]Van Speybroeck, V.; Van der Mynsbrugge, J.; Vandichel, M.; Hemelsoet, K.; Lesthaeghe, D.; Ghysels, A.; Marin, G. B.; Waroquier, M. J. *Am. Chem. Soc.* 2011, 133, 888.

[3]Svelle, S.; Tuma, C.; Rozanska, X.; Kerber, T.; Sauer, J. J. *Am. Chem. Soc.* 2009, 131, 816.

[4]Svelle, S.; Visur, M.; Olsbye, U.; Saepurahman; Bjorgen, M. *Top. Catal.* 2011, 54, 897.

3. Provide an abstract (10 lines) for scientific communication on the website in layman's terms. See also item 13 of this application form.

No abstract of this work may be published on the website (see item 13).

Alkene methylation is a crucial reaction during the MTO conversion in zeolites. A thorough benchmark on these reactions with MD-based techniques will be performed and the obtained kinetic results will be compared with available experimental and theoretical data.

4. Financing institution or channel, financing the research project in full or in part (FWO, BOF, IWT, EU, ...): Please attach the confirmation letter as enclosure (see instructions in enclosure 4 “EasyChair proposals submission procedure”).

European Research Council under the European Union’s Horizon 2020 research and innovation programme (consolidator ERC grant agreement No 647755 – DYNPOR (2015-2020))

5. Name and email address of the promoter(s) of the research project:

Prof. dr. ir. Veronique Van Speybroeck (Veronique.VanSpeybroeck@UGent.be)

6. Billing address to which the payment invoice will be sent to:

Prof. dr. ir. Veronique Van Speybroeck
Center for Molecular Modeling (CMM)
Technologiepark 903
9052 Zwijnaarde

7. Persons mandated by the Applicant to compute on the Tier1 within the framework of the present project: Please provide for every person:
 - name and first name
 - institution
 - research group / department
 - title / position
 - experience of using HPC resources in the past (Tier0/Tier1/Tier2 infrastructure in Belgium and abroad)

Dr. ir. Kristof De Wispelaere
Ghent University, Center for Molecular Modeling
ERC Postdoctoral researcher
2 years of experience with TIER1 at Ghent University
½ year of experience with TIER1 and TIER2 in The Netherlands
5 years of experience with TIER2 at Ghent University

Ir. Simon Bailleul
Ghent University, Center for Molecular Modeling
ERC PhD fellow
1 month of experience with TIER1 at Ghent University
1 year of experience with TIER2 at Ghent University

Prof. dr. ir. Veronique Van Speybroeck
Ghent University, Center for Molecular Modeling
Full Professor

6 years of experience with TIER2 at Ghent University

8. Explain why this project needs to run on a Tier1 system, why the machine you have requested is suitable for the project and how the use of the system will enable the science proposed (max. ½ A4 in Arial 12).

The application of advanced molecular dynamics simulations in the field of heterogeneous catalysis is emerging. The Center for Molecular Modeling was one of the first research groups to succeed in applying metadynamics for the prediction of kinetics of zeolite-catalyzed reactions.[Moors, S. L. C. et al. ACS Catal. 2013, 3, 2556; Van der Mynsbrugge, J. et al. ChemCatChem 2014, 6, 1906; De Wispelaere, K. et al. Chem. Eur. J. 2015, 21, 9385.] To strengthen our position as pioneers we need to make some more substantial contributions with high impact to this highly competitive field. In this view the involved researchers are in need of access to the highly efficient TIER1 infrastructure.

The total number of jobs included in this research project is estimated to be 59, however to obtain accurate results, the simulations need to be well-equilibrated and long simulation times are required to achieve statistically relevant data. Therefore, the TIER1 infrastructure can significantly speed up this research. The need for long AIMD simulations retains the widespread use of this kind of simulations in the area of zeolite-catalyzed reactions where AIMD simulations are indispensable to accurately describe some crucial effects during heterogeneously catalyzed reactions.

9. Justify the number of node days requested. This should include information such as: number and nature of computing tasks, software used, and the sequence in which they will be performed. Indicate for each typical computing task the required resources:

- wall clock time (note that 3 days is the maximal wall clock time for any job; checkpointing should be used for longer run times)
- memory (maximum 64 GiB/node)
- number of nodes
- number of CPU cores

- disk space (estimated volume in GiB and the total number of files); make a clear distinction between usage of Tier2 DATA/HOME partitions and the Tier1 SCRATCH partition
- number of tasks, and an indication of how many such tasks would be submitted concurrently.

This information should take the form of a table (an example is provided as Table 2 in the appendix). Provide additional descriptions of the computing tasks and comments as needed. Resource estimates should be preferably based on the results of actual calculations on Tier1 (via, e.g., a Starting Grant) for system/problem sizes that are on par with those of the intended computing tasks (e.g., same mesh sizes, actual molecular system, ...). If not, provide the name, architecture, #cores, memory, etc. of the machine that was used to obtain these results and explain how you have calculated/rescaled the wall clock times, number of cores, etc.

(max. 1 A4 Arial 12).

Three types of Ab initio molecular dynamics (AIMD) based simulations will be performed with the CP2K software package on systems consisting of approximately 300 atoms. The computational requirements for this study have been carefully considered based on test simulations on the systems under study performed on the TIER2 (delcatty cluster) and TIER1 infrastructure at Ghent University.

Calculation flow:

1. Molecular dynamics (MD) simulations in the NPT ensemble at 623 K and 1 atm for 50 ps are required to study the behaviour of the reactants in the zeolitic environment at high temperature. For ethene these simulations will be performed with and without BJ damping. Once the influence of the damping is clarified, one scheme will be selected to study the co-adsorption of the other alkenes. The total number of MD jobs is thus 7.
2. Metadynamics (MTD) simulations in the NVT ensemble at 623 K typically take around 100 ps to yield converged results. Similarly as for the MD simulations, the total number of MTD simulations is 7.
3. Constrained dynamics (CMD) simulations in the NVT ensemble at 623 K will be used to calculate forces acting on well-chosen collective variables. Consequently, thermodynamic integration of these forced yields the free energy. We estimate that around 15

points along each reaction path will have to be selected for a CMD run of 25 ps. Initially, the CMD simulations will only be applied to ethene (with and without BJ damping) and propene methylation. The total number of CMD simulations is thus 45.

Table 1 summarizes the estimated node and core days required for each simulation type:

Table 1. Estimated core and node days required for the project.

Job type	# of simulations	Node days per simulation	Total node days	Total core days
MD	7	52	364	5824
MTD	7	55	385	6160
CMD	45	14	630	10080
			1379	22064

Table 2 summarizes the requirements for scratch space and long-term storage for each simulation type. Because of the long simulation times, a complete MD or MTD trajectory cannot be obtained within the wall time limit of 72 hours, but requires several restarts. As a result, the scratch volume per MD, MTD or CMD simulation is relatively low.

Table 2. Estimated scratch space and long-term storage requirements for the project.

Job type	Scratch [GB/run]	Long-term storage [GB/run]	Total scratch [GB]	Total long-term storage [GB]
MD	0.5	10	$7 \cdot 0.5 = 3.5$	$7 \cdot 10 = 70$
MTD	0.5	20	$7 \cdot 0.5 = 3.5$	$7 \cdot 20 = 140$

CMD	0.5	5	$45 \cdot 0.5 = 22.5$	$45 \cdot 5 = 225$
			29.5	435

10. Describe the software required to perform the computing task(s). Please clearly provide the following per item in this regard:

- a reference to the software's web page
- the software license system (open source, GPL, etc.)
- if there is no free academic use of the software, state which license makes the installation and the use valid on the Tier1 by the Applicant (+ add a copy of the signed license)
- if need be, which license server will be used (name + IP address)
- whether the software is already available on the Tier1 (see <https://vscentrum.be/nl/Tier1-rekenen>) and, if this is not the case, compilation and installation instructions (possibly with reference to existing Tier2 installation)

Molecular dynamics simulations will be performed using the CP2K software package (<http://www.cp2k.org/>), which is freely available under the GPL license. The required version of the programme (CP2K/20130228-ictce-4.1.13) is already available on TIER1.

Provide the results of scaling tests that were conducted with this software, preferably on Tier1 (using, e.g., a Starting Grant) for system/problem sizes that are on par with those of the intended computing tasks (e.g., same mesh sizes, actual molecular system, ...). If not, provide the name, architecture, #cores, memory, etc. of the machine that was used to obtain these results.

Provide both a table and scaling plot such as table 1 and plot 1 in the appendix (max. 2 A4 in Arial 12).

Scaling of the CP2K software on the TIER1 has been tested for one of the systems under study, i.e. methanol and ethene adsorbed in H-ZSM-5 at 623 K and 1 atm. Short NPT runs (100 steps) have been performed on 16, 32, 64, 128 and 256 cores on the TIER1 cluster consisting of 16 core nodes and the average time per MD step was calculated as shown in

Figure 2. Additionally, Figure 3 displays the speedup normalized to 16 cores for these simulations. The use of more than 2 nodes does not efficiently speed up the simulation.

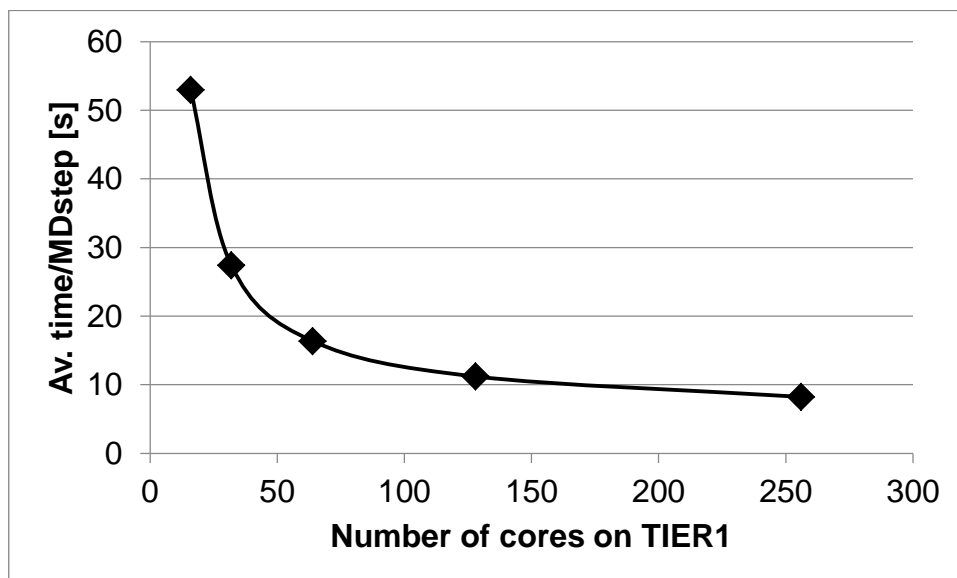


Figure 2. Average time per NPT MD step for methanol and ethene in H-ZSM-5 at 623 K and 1 atm with CP2K on TIER1 with 1-16 nodes.

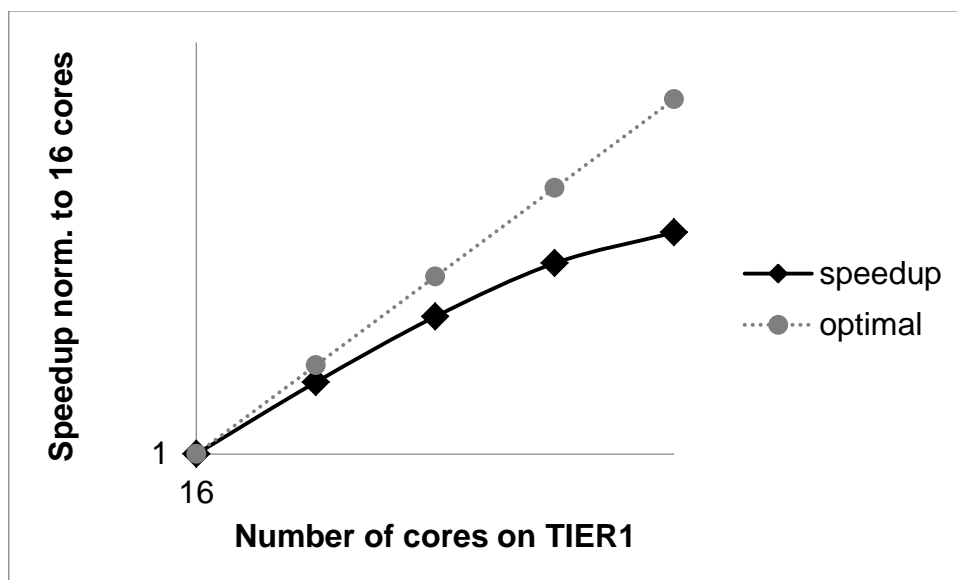


Figure 2. Speedup normalized to 16 cores for an NPT MD simulation of methanol and ethene in H-ZSM-5 at 623 K and 1 atm with CP2K on TIER1 with 1-16 nodes.

11. Describe how you will manage the resources requested in the period during which the task is to be performed. What usage pattern do you anticipate (similar usage on monthly basis, bursts, ...)?

We estimate the proposed simulations can be completed over a time period of **3 months**, preferably **starting in January 2016**. Similar usage on a monthly basis is expected.

This estimated timeframe takes into account the actual runtime of the simulations, as well as intermediate data analysis tasks and job restarts.

12. List the granted computing time allocations to the promoter(s) of this research project, on the Flemish Tier1 system, as well as other Tier1 and Tier0 systems. Also, describe the scientific output obtained within the framework of computing time that was granted during the past two years on the Flemish Tier1 or on other Tier1 or Tier0 supercomputers. DOI links are sufficient.

List of granted research projects on the Flemish Tier1 system:

- Dynamical kinetic study of zeolite catalyzed reactions (K. De Wispelaere, 4371 node days, 07/07/2014 – 31/12/2014)
- Exploring the kinetics and selectivity of butene cracking using molecular dynamics simulations (J. Van der Mynsbrugge, 4864 node days, 01/01/2015 – 30/06/2015)
- Characterizing adsorption properties of C₄ – C₆ alkenes on H-ZSM-5 using molecular dynamics simulations (P. Cnudde, 4260 node days, 13/07/2015 – 31/12/2015)

List of scientific output within the framework of granted computing time:

- Insight in the effect of water on the methanol-to-olefins conversion in H-SAPO-34 from molecular simulations and in-situ micro-spectroscopy, K. De Wispelaere, C.S. Wondergem, B. Ensing, K. Hemelsoet, E.J. Meijer, B.M. Weckhuysen, V. Van Speybroeck, J. Ruiz-Martinez, ACS Catalysis, Submitted, 2015
- <http://dx.doi.org/10.1002/chem.201500473>
- <http://dx.doi.org/10.1016/j.jcat.2015.01.013>
- <http://dx.doi.org/10.1002/cctc.201402146>
- <http://dx.doi.org/10.1021/cs400706e>
- <http://dx.doi.org/10.1039/c4mh00127c>
- <http://dx.doi.org/10.1039/C3CP54132K>

13. Are the applicants of this application bound by a confidentiality agreement? If so, the title and the abstract of this application will not be published on the website of the Hercules Foundation / Flemish Supercomputer Center.

Yes

Should you have any questions or encounter any difficulties during the electronic submission of an Application, please contact by e-mail:
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For the other institutions: marc.luwel@herculesstichting.be