Enclosure 1b. Category 1 Application form – 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 English on the website
https://www.vscentrum.be/en/access-and-infrastructure/project-access-tier1

Title of the application:

Dynamical first principle modelling of zeolite dealumination in H-SSZ-13

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:

3624

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

156 GB scratch space – 972 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):

When zeolite catalysts are regenerated they are exposed to steam at high temperatures. This leads to irreversible dealumination of the zeolite - extraction of Al from the zeolite framework - which permanently reduces the activity of the catalyst.

The dealumination reaction is generally very complicated to model, because it involves sequential hydrolysis of four bonds between aluminum and oxygens of the zeolite framework, see Figure 1. Hence fundamental insight to the process is limited.
A deeper understanding of dealumination could help to determine the most stable zeolite material toward steaming, and also explain why some T-sites apparently are resistive to steaming.

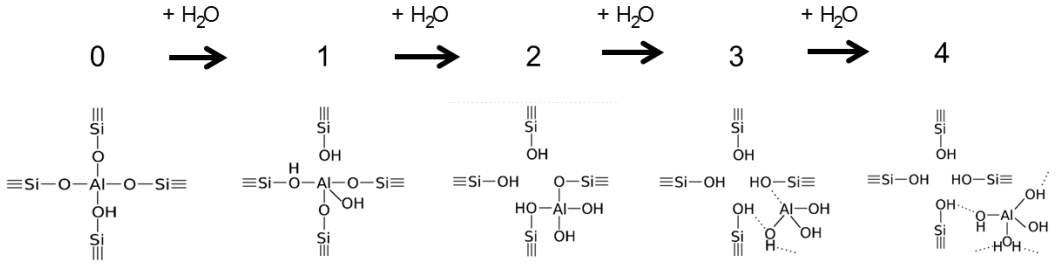

Figure 1. A simple diagram showing the four reaction steps of the dealumination reaction

As the first of its kind, a theoretical investigation of the dealumination process including energetic and kinetic modelling has been published recently [1]. This work was however based on calculation using static Density Functional Theory (DFT) calculations. As reaction conditions are typically at temperatures higher than 700 K, the harmonic limit for vibrations is a questionable approach, and the influence of more than one water molecule at a time is not included. First-principles molecular dynamics (MD) simulations are suited to model the reaction without the mentioned limitations [2].

The aim of this project is to employ advanced MD techniques to model the mechanism and kinetics of the dealumination reaction at operating conditions. Initially, calculations will be performed on the adsorbates without surrounding molecules; this allows comparing directly to the already available static results, in order to address the influence of anharmonicity, framework flexibility and multiple reaction paths. Next, a set of calculations at realistic conditions will address the role of the high temperature and the presence of multiple water molecules during the reactions.

[1] M. Nielsen, R. Y. Brogaard, H. Falsig, P. Beato, O. Swang, S. Svelle, *ACS Catal.*, **2015**, 5, 7131-7139

[2] Van Speybroeck, V.; Hemelsoet, K.; Joos, L.; Waroquier, M.; Bell, R. G.; Catlow, C. R. A. *Chem. Soc. Rev.* **2015**, 44, 7044.

3. Provide an abstract (10 lines) for scientific communication on the website in layman's terms. See also item 12 of this application form.

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

When zeolite catalysts are subjected to steam at high temperatures, a permanent loss of activity happens, because of the loss of aluminum from the framework. This dealumination is a complex process involving the hydrolysis of four Al−O bonds. This work addresses the dealumination from a theoretical point of view, modeling the kinetics in zeolite H-SSZ-13 with advanced molecular dynamics techniques. The envisaged detailed molecular-level understanding should also allow to extend to other zeolites. This insight will play a key role when designing catalysts, minimizing permanent loss of activity.

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. 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 (CMM)
ERC Postdoctoral researcher
2.5 years of experience with TIER1 at Ghent University
0.5 year of experience with TIER1 and TIER2 in The Netherlands
5.5 years of experience with TIER2 at Ghent University

M.Sc. Malte Nielsen
Guest researcher at CMM (08/08/2016 – 31/12/2016)
Department of Chemistry, University of Oslo
PhD Candidate
1.5 years of experience with TIER1 at University of Oslo
1.5 years of experience with TIER2 at Technical University of Denmark

Prof. dr. ir. Veronique Van Speybroeck
Ghent University, Center for Molecular Modeling
Full Professor
6.5 years of experience with TIER2 at Ghent University

7. 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).

Recently, advanced molecular dynamics (MD) techniques have been introduced in the field of heterogeneous catalysis. In this evolution, the Center for Molecular Modeling plays a key role due to our expertise in applying advanced MD simulations to study zeolite-catalyzed reactions [Moors et al. ACS Catal. 2013, 3, 2556; Van der Mynsbrugge et al. ChemCatChem 2014, 6, 1906; Van Speybroeck et al. Chem. Soc. Rev. 2014, 43, 7326; De Wispelaere et al. Chem. Eur. J. 2015, 21, 9385.] The present project for the first time extends the methods to reactions that modify the nature of the zeolite framework due to steaming. The complexity of this process makes a thorough computational resource demanding and needs of access to the highly efficient TIER1. Moreover, to maintain and strengthen our position as pioneers we need access to the

best available infrastructure. The need for long AIMD simulations retains the widespread use of this kind of simulations in the area of zeolite catalysis where AIMD simulations are indispensable to accurately describe realistic operating conditions of heterogeneously catalyzed reactions.

The total number of jobs included in this research project is estimated to be 312 and all jobs require a simulation time in the window of at least 50-150 ps to obtain accurate results. Indeed, the simulations need to be well-equilibrated and long simulation times are required to achieve statistically relevant data.

To obtain 1 ps of useful information from an MD simulation, a wall time (on a single node) of roughly 8h is required, depending on the system size. Therefore, the TIER1 infrastructure is crucial to achieve the goals of the project.

8. 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).

All MD simulations included in this proposal will be based on Density Functional Theory (DFT) and will be performed with the CP2K software package on systems consisting of approximately 110-150 atoms (depending on the loading of water molecules).

We distinguish three types of ab initio molecular dynamics (AIMD) simulations that will be performed within this project. The computational requirements for this study have been carefully considered based on test simulations on the systems under study performed on the TIER1 (muk) infrastructure (see point 10). The required number of node days per simulation was calculated based on the use of maximum 2 nodes per job (see point 10).

Calculation flow:

1. Molecular dynamics (MD) simulations in the NPT ensemble at 723 K and 1 atm with and without water molecules for 50 ps are required to get time-averaged unit cell parameters and well-equilibrated starting structures for the metadynamics simulations (*vide infra*). During these simulations, the number of water molecules per acid site in the SSZ-13 material will be gradually increased from 0 to 8. The total number of MD jobs is thus 4 * 9 = 36.
2. Metadynamics (MTD) simulations in the NVT ensemble at 723 K typically take at least 100 ps to yield converged free energy surfaces. These will be done for each of the four steps in the reaction, with 0-8 surrounding water molecules. The total number of MTD simulations is thus 4*9 = 36.
3. Umbrella Sampling (US) simulations in the NVT ensemble at 723 K will be used to verify the MTD results and obtain more accurate free energy barriers. For the four reaction steps, we estimate that we need 20 sampling points (umbrellas) and for each umbrella we will need MD simulations of approximately 20 ps. We will perform the umbrella sampling simulations on a system without additional water molecules, one with an intermediate and one with a high water loading. This means a total of 4 * 3 * 20 = 240.

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	36	18	648	10368

MTD	36	36	1296	20736
US	240	7	1680	26880
			3624	57984

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 US 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	5	36*0.5 = 18	36*5 = 180
MTD	0.5	10	36*0.5 = 18	36*10 = 360
Umbrella	0.5	1.8	240*0.5 = 120	240*1.8 = 432
			156	972

9. 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.

Scaling of the CP2K software on the TIER1 has been tested for one of the systems under study, the SSZ-13 catalyst loaded with a single water molecule at 723 K and 1 bar. 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. Figure 2 displays the speedup normalized to 16 cores for these simulations. It can be concluded that the use of more than 2 nodes does not efficiently speed up the simulations. The computational burden for MTD and US simulations (see point 8) is quite similar as for the MD simulations.

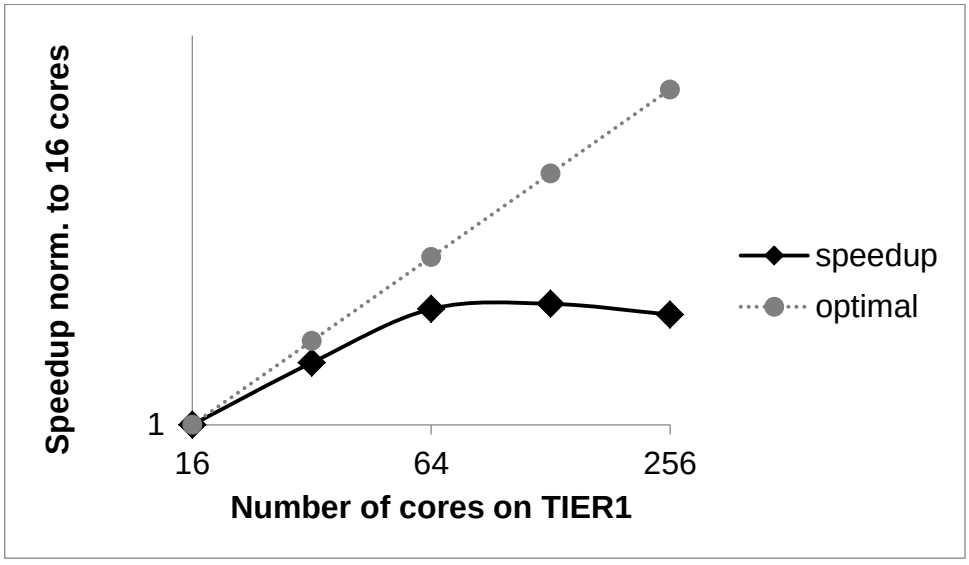

Figure 2. Speedup normalized to 16 cores for an NPT MD simulation of water in SSZ-13 at 723 K and 1 bar with CP2K on TIER1 with 1-16 nodes.

10. 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 **6 months**, preferably **starting in August 2016** (as soon as possible). 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.

11. 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 first principle modelling of ethene oligomerization in Ni-SSZ-24 (K. De Wispelaere, 3232 node days, 01/03/2016 – 31/08/2016)
- 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 C_4 – C_6 alkenes on H-ZSM-5 using molecular dynamics simulations (P. Cnudde, 4260 node days, 13/07/2015 – 31/12/2015)
- Dynamical first principle benchmark studies on alkene methylation in H-ZSM-5 (K. De Wispelaere, 1400 node days, 01/12/2015 – 30/06/2016)

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

- Suppression of Aromatic Cycle in Methanol-to- Olefins Reaction over ZSM-5 by post-synthetic modification using Calcium, I. Prokopyeva, S. Bailleul, A. Pustovarenko, J. Ruiz-Martínez, K. De Wispelaere, J. Hajek, B.M. Weckhuysen, K. Houben, M. Baldus, V. Van Speybroeck, F. Kapteijn, J. Gascon, Angew. Chem. Int. Ed., submitted, 2016
- J. Hajek, J. Van der Mynsbrugge, K. De Wispelaere, P. Cnudde, L. Vanduyfhuys, M. Waroquier, V. Van Speybroeck, J. Catal., 2016, in press
- http://dx.doi.org/10.1039/C5CY02073E
- http://dx.doi.org/10.1021/acscatal.5b02139
- 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

12. 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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