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:

Characterizing adsorption properties of C_4 – C_6 alkenes on H-ZSM-5 using molecular dynamics simulations

Name and first name of the applicant:

Cnudde Pieter

Institution:

Ghent University

Research group / department:

Center for Molecular Modeling

Title / position:

ir. / PhD Fellow

E-mail address:

Pieter.Cnudde@UGent.be

Total computing time that is needed, in node days:

4260

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

378 GB scratch space – 610 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:

"Functional Supramolecular Systems (FS2)" - IUAPVII/138 –
prof. dr. ir. Veronique Van Speybroeck

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):

H-ZSM-5 is a widely applied catalyst in the (petro)chemical industry for hydrocarbon conversion in methanol-to-olefins, catalytic cracking, hydrocracking, etc. In many of these processes, alkenes (and alkanes) are involved, which interact with the active site of the catalyst. Therefore, a proper understanding of alkene (and alkane) adsorption is crucial to further optimize reaction conditions and catalysts. Obtaining experimental information about the adsorption of olefins is difficult due to the high reactivity of alkenes, which are prone to oligomerization and isomerization reactions, even at low temperatures. To this end, molecular dynamics simulations at an actual process temperature of 500°C can be applied to elucidate the nature of the adsorbed alkenes. Upon adsorption of alkenes at the active site of the catalyst, three different intermediate states exist: a physisorbed alkene, a chemisorbed carbenium ion or a chemisorbed alkoxide. In this study, MD simulations will be applied on these three intermediate states for linear C_4 , C_5 and C_6 alkenes and branched C_4 and C_5 alkenes to evaluate their relative stability and to assess the effect of branching. For each linear alkene, 5 simulations need to be performed: on the 1-alkene, 2-alkene, alkyl cation, 1-alkoxide and 2-alkoxide species. For each branched species, 3 simulations will be performed: on the iso-alkene, t-alkyl and t-alkoxide species. Free energies and entropies will be evaluated by statistical averaging over a sufficiently long simulation. To study how the different stable adsorption states can convert into each other, Metadynamics (MTD) simulations will be applied. In total, 8 systems, connecting the different intermediates from the MD simulations, are under consideration (shown in Figure 1). From these MTD simulations, the free energy surface (FES) of the adsorbed species is reconstructed, and thermodynamic and kinetic data are inferred for the (trans)formation of these adsorption states. To validate the reliability of the MTD simulations,

a detailed committor analysis will be performed by generating hundreds of MD paths from the obtained FES.

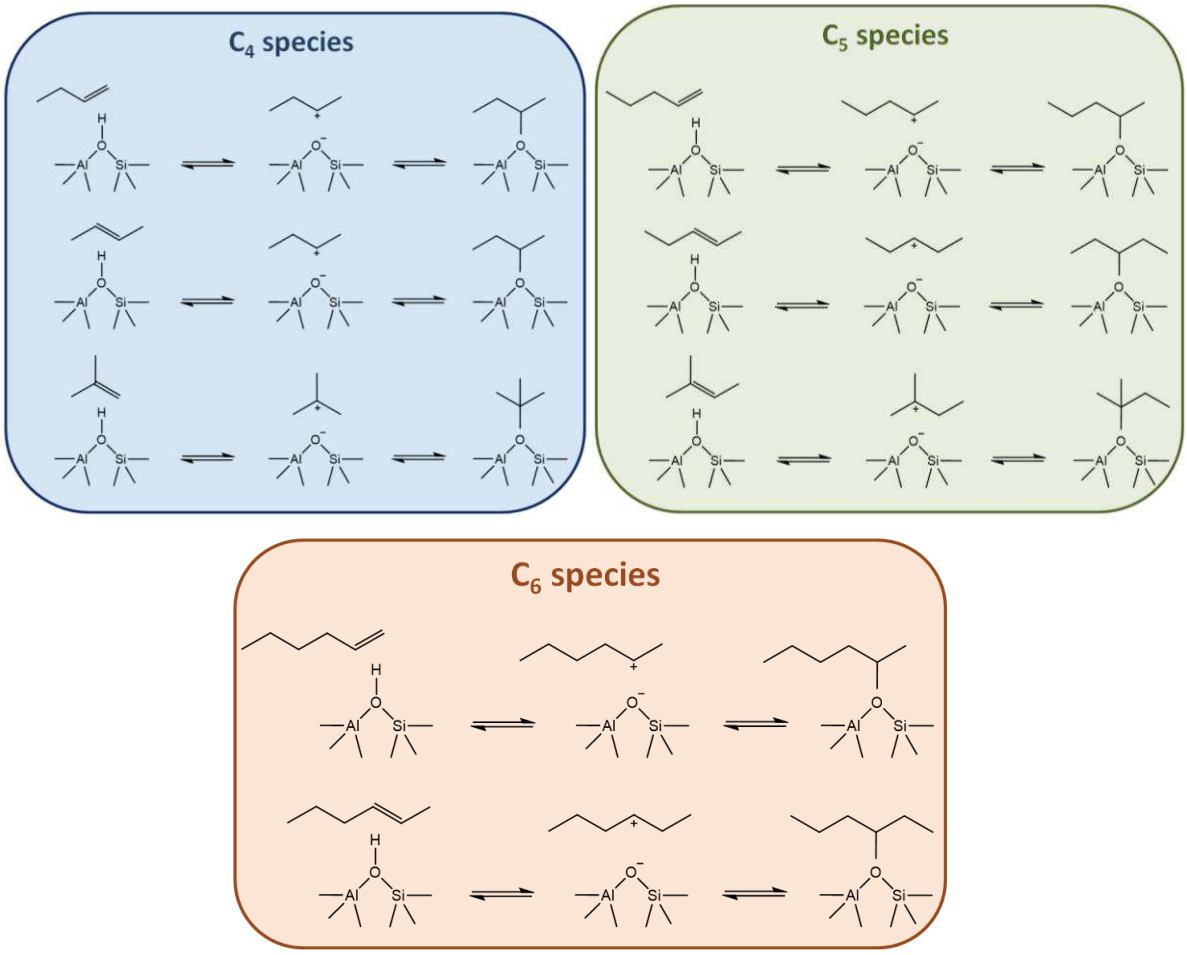

Figure 1. Schematic representation of the C_4 – C_6 alkene adsorption states and transitions between these states that will be studied.

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

   Catalytic cracking of C_4-C_6 alkenes over MFI catalysts is employed in industry to upgrade low-value product streams by increasing the light olefin yield. To further optimize these processes, a proper understanding of alkene adsorption is of the utmost importance. For example, it is still an open question how precisely the adsorbed species interact with the active site of the catalyst. In this work, the

dynamic behavior of various C_4-C_6 alkene species is investigated using ab initio molecular dynamics simulations at high temperature. With this technique, the free energy surface is sampled, taking into account conformational freedom and lattice flexibility.

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”).

“Functional Supramolecular Systems (FS2)” - IUAPVII/138 –
prof. dr. ir. Veronique Van Speybroeck (see attachment)

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)

Pieter Cnudde
Ghent University, Center for Molecular Modeling
PhD Fellow
½ year of experience with TIER1 at Ghent University
2 years of experience with TIER2 at Ghent University

Following researchers are actively involved in this project.

Jeroen Van der Mynsbrugge
Ghent University, Center for Molecular Modeling
BOF Post-doc
1 ½ year of experience with TIER1 at Ghent University
6 years of experience with TIER2 at Ghent University

Kristof De Wispelaere
Ghent University, Center for Molecular Modeling
FWO-PhD Fellow
1 ½ year of experience with TIER1 at Ghent University
½ year of experience with TIER1 and TIER2 in The Netherlands
4 ½ years of experience with TIER2 at Ghent University

Veronique Van Speybroeck
Ghent University, Center for Molecular Modeling
Full Professor
1 ½ year of experience with TIER1 at Ghent University
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).

Due to the quite large system, containing ca. 300 atoms, completing the proposed simulations within a reasonable timeframe requires performing multi-node jobs on at least 4 nodes in parallel. Furthermore, execution of these jobs will include several restarts and will require more than 4000 node days computing time in total. The ability to run a large amount of multi-node jobs simultaneously on the TIER1 infrastructure will be indispensable for this project. The large number of simulations and the long simulation times required for attaining statistically relevant data has long prohibited the application of molecular dynamics methods to the study of zeolite-catalyzed reactions, but nowadays the application of advanced molecular dynamics simulations in heterogeneous catalysis research is quickly gaining momentum. The Center for Molecular Modeling was among the first research groups to successfully apply metadynamics for studying the mechanism and kinetics of zeolite-catalyzed reactions (S.L.C. Moors et al, *ACS Catal.*, 2013, 2556-2567; J. Van der

Mynsbrugge, et al., *ChemCatChem*, 2014, 1906-1918). Access to the highly efficient TIER1 infrastructure with its fast nodes and inter-nodal communication would enable us to make further high-impact contributions to this highly competitive field.

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).

Large-scale ab initio molecular dynamics (AIMD) simulations will be performed with the CP2K software package, using MPI. No vSMP system will be used.

Three types of simulations will be performed. The computational requirements for this study have been carefully considered, based both on test simulations performed on the TIER2 infrastructure at Ghent University (delcatty cluster) and on simulations of the TIER1 project “Exploring the

kinetics and selectivity of butene cracking using molecular dynamics simulations" on the TIER1 infrastructure at Ghent University.

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

- For the **21** different configurations (C_4-C_6 adsorption states), **MD simulations** in the NVT ensemble at 500°C with an average duration of 150 ps will be performed to determine the thermodynamic properties (entropy, free energy, …) of each species. Sufficiently long simulations are required to obtain accurate statistical averages. The system under study consists of an H-ZSM-5 unit cell with 289 atoms and guest molecules with 9 to 13 atoms. MD simulations of comparable systems on TIER1 (from our previous TIER1 project: "Exploring the kinetics and selectivity of butene cracking using molecular dynamics simulations") have shown that 15 ps simulations require approximately 10 node days (multi-node jobs on 4 nodes). Therefore, it is expected that each of these simulations will require about **100 node days**.
- To analyse the interconversion between the different possible adsorption states, **8 MTD simulations on the alkoxide – carbenium ion – alkene transition** will be performed (The 3 linear species require 2 MTD simulations each; the 2 branched species require 1 simulation each). Typical simulation times amount to 100 – 200 ps, depending on the height of the free energy barrier of the reaction and the number of collective variables required to consider in the simulation. Based on test simulations performed on delcatty and previous experience with MTD simulations on analogous systems, each simulation is expected to take up approximately **120 node days**. Again multi-node jobs using 4 nodes will be performed.
- To assess the quality of the results obtained from the MTD simulations, a **committor analysis (CA)** will be performed by generating hundreds of AIMD paths starting from the trajectory of each of the **8** MTD runs. Based on test simulations performed on delcatty, the time to generate 1 path is estimated to be about **18 node hours** for systems with unit cells as large as H-ZSM-5. To obtain sufficient sampling for statistical relevant results, it is estimated that at least **200 paths** will have to be generated for each of the MTD runs.

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	21	100	2100	33600
MTD	8	120	960	15360
CA	8	200 x 0.75	1200	19200
			4260	68160

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 of MTD 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	2	10	21*2 = 42	21*10 = 210
MTD	2	10	8*2 = 16	8*10 = 80
CA	0.2	0.2	8*200*0.2 = 320	8*200*0.2 = 320
			378	610

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 thoroughly tested by pilot user Andy Van Yperen–De Deyne. These tests have demonstrated that excellent scaling is obtained up to 64 cores for a system of similar size (Figure 2). Although the scaling test has been performed on a box of water molecules, similar results are expected for a zeolite unit cell since the scaling will be mainly determined by the number of atoms, the theoretical method (revPBE) and basis set (DZVP-GTH) that is used in the DFT calculations. The theoretical methodology and basis set used in this project are the same as used for the scaling test. The number of atoms of the zeolite system in this project amounts to ca. 300.

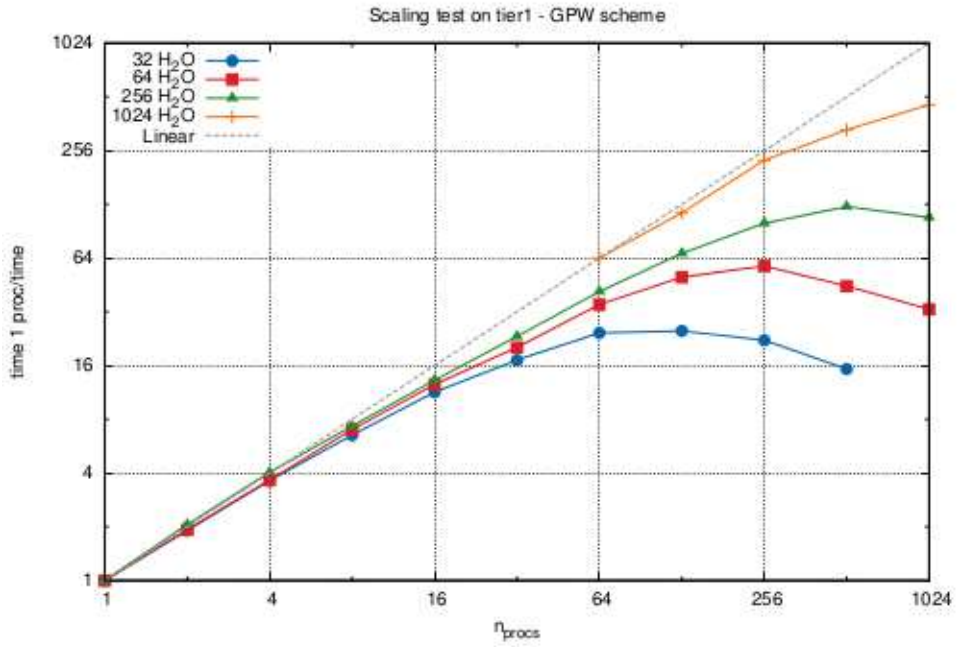

Figure 2. Efficiency vs. number of CPUs for various system sizes with the GPW code of CP2K.

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 approximately **6 months**, preferably **starting in July 2015**. 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 frequent 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 zeolite catalysis on the Flemish Tier1 system:

- Molecular dynamics study of pentene in H-ZSM-5: towards a better estimate of adsorption enthalpies (J. Van der Mynsbrugge – 1824 node days – 07/03/'14 – 06/07/'14)
- Dynamical kinetic study of zeolite catalyzed reactions (K. De Wispelaere – 07/07/'14 – 31/12/'14)
- Exploring the kinetics and selectivity of butene cracking using molecular dynamics simulations (J. Van der Mynsbrugge – 4864 node days – 01/01/'15 – 30/06/'15)

List of scientific output DOI's within the frame of TIER1 computing time on zeolite catalysis:

- 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

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Interuniversity Attraction Poles (IAP)
Phase VII

2012 - 2017

CONTRACT P7/05

ANNEX I - Section II

Information on the partner

To be completed by each network partner including the international partner(s)

Name of the partner: **Van Speybroeck Veronique** Institution: **Universiteit Gent**
Title of the project : Functional Supramolecular Systems
Acronym of the project : FS2

II. 8. BUDGET (per partner) *

(in EURO without decimals)

P7/05 - P11 (V.Van Speybroeck)	2012-2017
Personnel	399,533
Operating costs	59,334
Equipment	18,190
Overheads (max 5% P+O)	22,943
Subcontracting	
Subtotal	500,000
Int partner 1 [name A]	
Int partner 2 [name B]	
Int partner 3 [name C]	
Int partner 4 [name D]	

* This table should not be completed by the International partner(s) as their budget is mentioned in the budgetary table of the Belgian partner of the network responsible for the follow-up of the partnership

Double click to complete the table.

- Personnel: indexed gross remunerations; employer's social contributions; statutory insurance costs as well as any other compensation or allocation legally due in addition to the salary; the reimbursements for PhD and postdoctoral grant holders (exempt from tax and benefiting from social security). Personnel costs must account for minimum 60% of the total budget attributed to each partner of the network. The costs for the tax-free PhD grants and postdoctoral grants may not account for more than 60% of the total personnel costs. The partners with a total budget of less than 600.000 euros can exceed this limit.

- Operating costs: basic supplies and products for laboratory, workshop or office; documentation, travel and accommodation; use of computing facilities; software; telecommunications; maintenance and operation of equipment and, more generally, consumables; hosting of visiting foreign researchers.

- Equipment: acquisition and installation of scientific and technical appliances and instruments, including IT equipment placed with a unit price higher than 500 euros.

- Overheads: general expenses of the institutions covering, on an inclusive basis, administrative, telephone, postal, maintenance, heating, lighting, electricity, rental, material depreciation and insurance costs (the total amount for this heading may not exceed 5% of total personnel and operating costs).

- Subcontracting: costs incurred by a third party in order to perform tasks or provide services necessitating specific scientific or technical skills outside the normal framework of the institution's activities (the amount may not exceed 25% of the total budget). Each request for subcontracting needs an approval from the programme manager.

II. 9. EQUIPMENT

Indicate the equipment (with an estimation of the cost) that will be purchased from the IAP-budget for the coming years (2012-2016) and justify.

A small budget of 18190 Euro is foreseen for purchase of small workstations.

II. 10. SUBCONTRACTING

To be completed only if subcontracting is foreseen.

Describe and justify the tasks and/or services that will be provided by a third party from outside the institution.