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SEVENTH FRAMEWORK PROGRAMME

ERC GRANT AGREEMENT No 240483

PROJECT TITLE KINPOR

Support for frontier research (ERC)

ERC Starting Grant

The **European Research Council Executive Agency** (the "*Agency*"), acting under powers delegated by the Commission of the European Communities (the "*Commission*")

of the **one part**,

and UNIVERSITEIT GENT, established in SINT PIETERSNIEUWSTRAAT 25, GENT, 9000, Belgium represented by Paul Van Cauwenberge, Rector and/or Luc Moens, Vice-Rector or their authorised representative, (the *beneficiary*),

of the **other part**

HAVE AGREED to the following terms and conditions including those in the following annexes, which form an integral part of this *grant agreement* (the "*grant agreement*").

Annex I - Description of Work
Annex II - ERC General Conditions - Single Beneficiary
Annex III - ERC accession forms for new and other *beneficiaries* to the *grant agreement.*
Annex IV - Financial statement form.
Annex V - a) 'Terms of reference for the certificate for the financial statements' and
b) 'Terms of reference for the certificate on the methodology'

Article 1 - Scope

The *European Community* has decided to grant a financial contribution for the implementation of the *project* as specified in Annex I, called *First principle chemical kinetics in nanoporous materials* (*KINPOR*) (the "*project*") within the framework of the *SP2-Ideas* and under the conditions laid down in this *grant agreement.*

Article 2 - The *principal investigator*

1. The "*principal investigator*" as defined in Annex II is Prof. Veronique Van Speybroeck, born in Ghent, Belgium, on 30/08/1974.

2. The *beneficiary* shall enter into a *supplementary agreement* with the "*principal investigator*". The provisions of the *supplementary agreement*, which are not in accordance with this *grant agreement*, shall be deemed to be void for the purposes of this *grant agreement.*

3. Together with the signed *grant agreement* the *beneficiary* shall transmit to the *Agency* a signed copy of this *supplementary agreement.*

Article 3 - Duration and *start date* of the *project*

The duration of the *project* shall be 60 months from 1st January 2010 (hereinafter referred to as the "*start date*").

Article 4 - Reporting periods and language of reports

1. The *project* is divided into scientific reporting periods of the following duration:

- PA: from month 1 to month 30
- PB: from month 31 to the last month of the *project.*

Any scientific report required by this *grant agreement* shall be in English.

2. The *project* is divided into financial management reporting periods of the following duration:

- P1: from month 1 to month 18
- P2: from month 19 to month 36
- P3: from month 37 to month 54
- P4: from month 55 to the last month of the *project.*

Any financial management report required by this *grant agreement* shall be in English.

Article 5 - Maximum *Community* financial contribution

1. The maximum *Community* financial contribution to the *project* shall be EUR 1,150,000.00 (*one million one hundred and fifty thousand EURO*). The actual *Community* financial contribution shall be calculated in accordance with the provisions of this *grant agreement.*

2. The *Community* financial contribution shall be in the form of a grant to the budget as specified in the table indicating the estimated breakdown of budget included in Annex I.

3. The bank account of the *beneficiary* to which all payments of the *Community* financial contribution shall be made is:

Name of account holder: Universiteit Gent
Name of bank: ING België
Account reference: BE59390096580026

Article 6 - Pre-financing

1. A pre-financing of EUR 460,000.00 (*four hundred and sixty thousand EURO*) shall be paid to the *beneficiary* within 45 days following the date of entry into force of this *grant agreement.*

2. The *beneficiary* hereby agrees that the amount of EUR *57,500.00* (*fifty-seven thousand five hundred EURO*), corresponding to the *beneficiary's* contribution to the Guarantee Fund referred to in Article II.20 and representing 5% of the maximum *Community* financial contribution referred to in Article 5.1, is transferred in their name by the *Agency* from the pre-financing into the Guarantee Fund. However, the *beneficiary* is deemed to have received the full pre-financing referred to in the first indent and will have to justify it in accordance with this *grant agreement.*

Article 7 - Special clauses

The following special clauses apply to this *grant agreement*:

Special clause 6

Notwithstanding the provisions of Article 6 the pre-financing shall be paid not earlier than 45 days before the *start date* of the *project.*

Article 8 - Communication

1. Any communication or request concerning the *grant agreement* shall identify the *grant agreement* number, the nature and details of the request or communication and be submitted to the following addresses:

For the *Agency*: European Commission
European Research Council Executive Agency
ERC Executive Agency - C2, COV2
Rue de la Loi 200
B-1049 Brussels, Belgium

For the *beneficiary*: Nathalie Vandepitte
UNIVERSITEIT GENT
Central administration
Sint-Pietersnieuwstraat 25
Gent 9000
Belgium

2. For information or documents to be transferred by electronic means, the following addresses shall be used:

For the *Agency*: For reports: the IT web system accessible via participants' portal: for financial statements (Form C) – system FORCE, for scientific reports SESAM. For any other information and documents: ERC-C2@ec.europa.eu

For the *beneficiary*: EU-cel@UGent.be

3. In case of refusal of the notification or absence of the recipient, the *beneficiary* is deemed to have been notified on the date of the latest delivery, if notification has been sent to one of the addresses mentioned in paragraphs 1 and 2 and to its legal representative.

4. Any communication or request relating to the processing of personal data (Article II.13) shall be submitted, using the address(es) for the *Agency* identified in paragraphs 1 and 2, to the Controller responsible for the processing: Head of Department "Grant Management"

Article 9 - Applicable law and competent court

The *Community* financial contribution is a contribution from the *Community* research budget with the aim to implement the 7th Research Framework Programme (FP7) and it is incumbent on the *Agency* and the *Commission* to execute FP7. Accordingly, this *grant agreement* shall be governed by the terms of this *grant agreement*, the *Community* acts related to FP7, the Financial Regulation applicable to the general budget and its implementing rules and other *Community* law and, on a subsidiary basis, by the law of Belgium.

Furthermore the *beneficiary* is aware and agrees that the *Commission* may take a decision to impose pecuniary obligations, which shall be enforceable in accordance with Article 256 of the Treaty establishing the *European Community*.

Notwithstanding the *Commission's* right to adopt directly recovery decisions referred to in the previous paragraph, the Court of First Instance or, on appeal, the Court of Justice of the European Communities, shall have sole jurisdiction to hear any dispute between the *Community* and a *beneficiary* concerning the interpretation, application or validity of this *grant agreement* and the validity of the decision mentioned in the second paragraph.

Article 10 - Application of the *grant agreement* provisions

Any provision of this part of the *grant agreement*, shall take precedence over the provisions of the Annexes and the provisions of Annex II shall take precedence over the provisions of Annex I.

The special clauses set out in Article 7 shall take precedence over any other provisions of this *grant agreement.*

Article 11 - Entry into force of the *grant agreement*

This *grant agreement* shall enter into force after its signature by the *beneficiary* and the *Agency*, on the day of the last signature.

Done in two originals in English.

For the *beneficiary* done at GENT

Name of the legal entity V. VAN SPEYBROECK
UNIVERSITEIT GENT

PROF. PAUL VAN CAUWENBERGE
Name of the legal representative

Stamp of the organisation (if applicable)

Signature of legal representative

21 SEP. 2009
Date

GEZIEN EN GOEDGEKEURD
24 SEP. 2009
YANNICK DE CLERCQ
REGERINGSCOMMISSARIS

For the *Agency* done at Brussels

Jack METTHEY
Director ad interim
Name of the legal representative

Signature of legal representative

30. 09. 2009
Date

European Research Council

SEVENTH FRAMEWORK PROGRAMME

"Ideas" Specific programme

European Research Council

Grant agreement for: Starting Grant

Annex I - "Description of Work"

Project acronym: KINPOR

Project full title: First principle chemical kinetics in nanoporous materials

Grant agreement no.: 240483

Date of preparation of Annex I (latest version): 26/08/2009

Principal Investigator: Veronique Van Speybroeck

Host Institution : Universiteit Gent

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Research proposal (Part B1)

Research proposal (Part B2)[1]

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[1] Instructions for completing Part B2 can be found in the Guide for Applicants on ERC Grant Schemes

ERC Starting Grant

Research proposal (Part B1)[2]

First principle chemical **kinetics** in nanoporous materials
KINPOR

Cover Page:

- Veronique Van Speybroeck (PI)
- Ghent University (Belgium)
- First principle chemical kinetics in nanoporous materials
- KINPOR
- 60 months

The design of an optimal catalyst for a given process is at the heart of what chemists do, but is in many times more an art than a science. The quest for molecular control of any, either existing or new, production process is one of the great challenges nowadays. The need for accurate rate constants is crucial to fulfil this task. Molecular modelling has become a ubiquitous tool in many fields of science and engineering, but still the calculation of reaction rates in nanoporous materials is hardly performed due to major methodological bottlenecks.
The aim of this proposal is the accurate prediction of chemical kinetics of catalytic reactions taking place in nanoporous materials from first principles. Two types of industrially important nanoporous materials are considered: **zeotype materials** including the standard alumino-silicates but also related alumino-phosphates and the fairly new **Metal-Organic Frameworks** (MOFs). This class of materials in which organic and inorganic moieties are linked, have astonished the zeolite community by their giant pores and huge surface area.
In this proposal new **physical models** are proposed to determine :
(i) **accurate reaction barriers** that take into account long range host/guest interactions and
(ii) the **preexponential factor** within a harmonic and anharmonic description, using cluster and periodic models and by means of static and dynamic approaches. Models to account for the breathing effect in which the pores can undergo drastic volume reductions/expansions in terms of strong host-guest interactions, are proposed.
The applications are carefully selected to benchmark the influence of each of the methodological issues on the final reaction rates. For the zeotype materials, reactions taking place during the Methanol-to-Olefin process (MTO) are chosen. A typical MTO catalyst is composed as an inorganic cage with essential organic compounds interacting as a supramolecular catalyst. For the hybrid materials, firstly accurate interaction energies between xylene based isomers and MOF framework, will be determined. The outcome serves as a step-stone for the study of oxidation reactions in vanadium based MOFs
The determination from first principles of chemical kinetics in nanoporous materials taking into account the actual material topology and composition has never done before and this proposal creates perspectives for the design of tailor made catalyst from the molecular level.

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[2] Instructions for completing Part B1 can be found in the Guide for Applicants on ERC Grant Schemes

Section 1a: The Principal Investigator

I Scientific Leadership Profile (max 2 pages)

I started my PhD in 1997 at the Laboratory of Subatomic and Radiation Physics. This Laboratory had a strong tradition in performing research in nuclear physics and interacting many body problems. I was the first PhD student in a new research line focusing on molecular systems. I was inspired by this new application field during a three-month visit at DSM Research in the Netherlands, immediately after my Master Studies. I worked there with a renowned scientist Prof. Dr. Robert Meier. Together with Prof. Dr. F. Buda (who is currently at the University of Leiden), he reported for the first time full dynamics, at a quantum mechanical level, of a catalytic chemical reaction (R.J. Meier et al., Ab-Initio Molecular-Dynamics Study Of Metallocene-Catalyzed Ethylene Polymerization, J. Am. Chem. Soc., 116, 7274). Despite my physical background, I was intrigued by the fascinating applications situated in the interdisciplinary field of physics and chemistry, within an industrial environment. This experience was very instructive and helped me in becoming familiar with both the academic and the industrial state of the art at that time. I created opportunities for the establishment of an international network. Moreover as I was embedded in an industrial research institute, I had to develop communication skills to work with researchers not belonging to my own discipline..

I had to be independent and self-propelling to a large extent to initiate the new research line from scratch at the Ghent University. New simulation techniques that were uncommon to my research department had to be studied and introduced. After four years, I obtained my PhD which reached an international quality level. This is measured by 10 publications in journals that are ranked as top journals in the physical chemistry community. I achieved to publish in Journal of the American Chemical Society (IF=7.885), the highest American Impact Journal in the interdisciplinary field of chemistry. This can be regarded as a spectacular achievement for somebody with a theoretical physics background. My strong communication skills with experimentalists and chemists, not belonging to my own research discipline, were a key factor for these major achievements.

Since then, my research was focussed on the development of new physical models applied to chemical problems of industrial interest. The combination of my physics background and my ability to use it to explore new research disciplines, were the key ingredients in going beyond state of the art. An illustration is my original work on internal rotors performed during my PhD, in which I presented a new physical model to treat conformational flexibility of large macromolecules. The software developed at that time is nowadays used by various international research labs and all the papers published from that work have received many citations. It also drew attention of a European EUROKIN network ("a European cooperation initiative on kinetics research") which is sponsored by nine companies and six universities. Additional funding was received from this network, to apply my software to chemical problems of industrial interest.

During my postdoctoral period, I got the opportunity to work independently and I was driven to attract new students to the new research entity that I initiated at the Ghent University. I was quite successful in attracting students and besides my own research activities; I was actively involved in the daily supervision of PhD students. Up to date this has already lead to four accomplished Ph.D theses of which I was supervisor [(i) Influence of low-vibrational modes on molecular partition functions and derived quantities from first principles, Peter Vansteenkiste, June 2006; (ii) Assessment of reactivity descriptors for the study of chemical reactions, Karen Hemelsoet, march 2007; (iii) Theoretical insight into the propagation kinetics and defect formation of free radical polymerization, Karen Van Cauter, May 2007; (iv) Unraveling the reaction mechanism of industrial processes in zeolite catalysis : A quantum mechanical approach, David Lesthaeghe, May 2007].

In 2001, I co-founded the Center of Molecular Modeling (http://molmod.ugent.be/) that is now composed of approximately 20 researchers. Within this center, I am leading the "Computational Molecular

Modeling on Industrial Processes" division, that consists of 3 postdocs, 6 PhD students and three Master Students. Some research subjects combine theoretical and experimental work resulting to shared PhD theses with experimental groups. These joint initiatives illustrate the increasing importance of interdisciplinary collaborations for my research field. In order to establish the transfer of knowledge to my own research team, I have attracted a post-doc from a top institute, i.e. the research group of Prof. Ken Houk from the UCLA. This demonstrates my capabilities to initiate new projects, to attract good quality new researchers to work in my research group, to promote innovative ideas, and to motivate people.

My track record proves that I embrace new ideas and challenges and I am always on the lookout for interesting collaborators across my chosen research field. The resulting science is very good when measured from the quality of chemical and physical journals in which my research is published (90 papers in peer-reviewed journals to date). Furthermore, the number of pretty different chemical problems I got involved in makes the work quite more impressive. For most of the papers I conceived the ideas, performed all simulations and implementations, established the collaborations and wrote the papers.

Particularly important for this project is my recent work on the methanol-to-olefin (MTO) process, a green catalytic route for the production of light olefins. Methanol is fed into a microporous zeolitic material producing olefins. The true nature of the reaction mechanism in the MTO process has been extremely controversial the last couple of decades, making it one of the most studied problems in catalysis. Together with one of my PhD students, I proved on basis of theoretically determined rate constants that all direct mechanisms that were believed for more than thirty years were impossible. This work was published as a Very Important Paper in the Angewandte Chemie – International Edition 45/2006. This is the top European Journal in the interdisciplinary field of chemistry (IF=10.031). This work attracted the attention of a renowned experimentalist in this field, Prof. Jim Haw, of the University of Southern California. A new collaboration with the USC Research group was initiated and I spend a couple of short visits at his Institute. The cross pollination between his experimental work on the MTO process and my theoretical research on the kinetics of individual reactions taking place in the microporous zeolite, resulted in two other publications in Angewandte Chemie the last two years.
The fact that I was able to calculate reaction rates in zeotype materials taking into account the topology of the material, is groundbreaking and was never done before in literature. The publication of three Angewandte Chemie papers over the last three years in this subject is a major achievement of my research team. I was able to go one step further than what was commonly done in literature, because new physical ingredients were implemented in available software. By communicating with the experimentalists, I could figure out very efficiently what were hot topics to apply my new methodologies on. The roadmap followed for this research topic is prototypical for the research conducting in my group.

I am currently the leader of the "Computational Molecular Modeling on Industrial Processes" division, which is made up of myself, 3 postdocs, 6 PhD students and three Master Students. This will provide a solid platform for undertaking my proposed programme of research. If successful with this Starting Grant I will, together with members of my research team, continue to apply to other external funding sources to further extend our research activities and to provide perspectives for our new research beyond the end of the ERC funding period.

ii Curriculum Vitae (max 2 pages)

Veronique Van Speybroeck
Born 30th August 1974
Nationality : Belgian
Personal Status : Married and mother of two children (Marcus and Alexander)
Date of PhD Award : October 2001

Study and PhD:

In 1997 I obtained my master degree in physical engineering from the Ghent University with great distinction. At the beginning of my PhD study I spent three months at DSM Research in the Netherlands to unravel theoretical aspects of the Car Parrinello molecular dynamics method. I obtained a PhD at the Ghent University entitled "Study of chemical reactions with static and dynamic molecular methods". The content of my PhD was published in 10 papers that appeared in peer-reviewed journals of which some belong to the top journals in the interdisciplinary field in chemistry (Journal of the American Chemical Society, IF=7.885). My work brought physics and chemistry together in an interdisciplinary field with particular emphasis on an accurate prediction of chemical kinetics including new method developments. The software developed at that time has been distributed freely among academic partners and is currently used by several international research groups.

International Exposure :

In 2001, I received a postdoctoral fellowship from the National Fund for Scientific Research Flanders. Within this framework, I had the possibility to travel to various foreign institutes for short periods. I have spent various short visits in the USA (Prof. Dr. J. Haw, USC, California), Turkey (Prof. Dr. V. Aviyente, Bogacizi University), Switzerland (Prof. Dr. J. Hutter), Ireland (Prof. J. Simmie, Combustion Chemistry Center), and others. These visits were very intensive, but very productive, as they resulted to joint papers in high-impact journals (Angewandte Chemie – International Edition, IF=10.031, Chemical Society Reviews, IF=13.082, Journal of the American Chemical Society, IF=7.885). I subsequently received several offers for positions in prominent research institutes in both the US and Europe.

Current Position

Since October 2007, I have a permanent position at the Ghent University as Research Professor. These permanent positions are specially designed for young prominent researchers with high potential to become world-class scientists. The competition to get such position is very high as it concerns an international call (about 150 applicants for 6 positions).

Teaching :

Lecture of following Master Courses :
" Atomic and Molecular Physics" from October 2007 – present
" Simulations and Modeling on the nanoscale" from October 2006 – present
" Molecular Modeling" from October 2004 - present

International Recognition

I am author or co-author of 90 publications in peer-reviewed journals of several appeared in the highest impact journals in the broad field of chemistry (3 Angewandte Chemie – International Edition, 3 Journal of the American chemical Society, 1 Chemical Society Reviews, 1 Chemical Communication). I have published with a broad spectrum of researchers with various backgrounds and from various countries. I am co-author of 60 conference papers, have attended more than 20 international conferences and have given 15 contributed or invited lectures. I also participated in workshops at foreign institutes (Advanced Catalysis Engineering, 2003, organised by NIOK, The Netherlands Institute for Catalysis Research). I am reviewer for various ACS journals (including the *Journal of the American Chemical Society, Journal of Physical Chemistry A/B/C, Macromolecules, Journal of Organic Chemistry,*) and the following European journals (*Chemical Physics Letters, ChemPhysChem, Angewandte Chemie, etc.*) with a frequency rate of about four per month. I am senior member of the *American Institute of Chemical Engineers* (AICHE, *www.aiche.org*, life member of the *World Association of Theoretical and Computational Chemists (WATOC, http://www.ch.ic.ac.uk/watoc/)* and member of the *American Chemical Society (ACS, www.acs.org)*.

Networks in Academia and Industry

I have a strong international network with leading scientist from all over the world (Prof. Leo Radom, School of Chemistry, Australia; Prof. Jim Haw, USC, USA, Prof. Viktorya Aviyente, Bogazici University, Turkey; Prof. Paul Ayers, Mc. Master University, Canada; Prof. Rutger Van Santen, TU Eindhoven, the Netherlands; Prof. Dr. B. Brooks, NIH, USA, Prof. Dr. J. Hutter, Switserland, Prof. Dr. R.J. Meier). All of these collaborations have led to common research papers which are already published or in press.

I have close contacts with several industrial partners and have given a lot of presentations of my research work at industrial meetings in research divisions of international companies. I have already completed several specific projects funded by industrial partners such as the EUROKIN network "a European cooperation initiative on kinetics research" sponsored by nine companies and six universities (http://www.dct.tudelft.nl/eurokin/).

Current Research Group

I was co-founder in 2001 of the Center for Molecular Modeling (CMM – http://molmod.ugent.be) which is currently composed of about 20 researchers. In this Center, I am leading the "Computational Molecular Modeling on Industrial Processes" division, that consists of 3 postdocs, 6 PhD students and three Master Students. I was supervisor of four PhD theses that were defended in 2006 and 2007.

Funding ID :

Several research projects have granted to me since my appointment as Research Professor in 2007. These include grants for hosting postdocs from international renowned institutes for a short period, enabling a transfer of knowledge into my research team. In all of them leading academic and industrial partners are involved. I was also involved in four other projects that were granted to the CMM.

Financing Agency	Period	Title	Budget In Euros
Ghent University (BOF- N24)	1/10/2007-30/9/2011	Kinetic models for industrially important chemical processes	170.000
Ghent University (BOF – visiting postdoctoral fellow)	Visiting postdocgrant for 3 mths	Modeling conducting polymers	12.412 Dr. A. Ozen (Istanbul)
Fund for Scientific Research Flanders (FWO-PhD fellowship)	1/10/2005-30/9/2009	Toetredingen tot gefunctionaliseerde 1,3-diazepine-2,4-dionen via ringexpansie en studie van hun reactiviteit	Salary for four years PhD (Candidate : D. Claeys)
Strategic Basic Research program – IWT (SBO-IWT)	1/11/2008-31/3/2013	In silico materials design and experimental validation for novel optical coatings	360.000 (part CMM)
Ghent University BOF-PhD fellow	1/10/2008-30/9/2012	Rational design of microporous catalysts guided by molecular modeling	Salary for four years PhD (E.Naziga)
FWO-postdoctoral position	1/10/07 – 30/9/10	Ab initio investigation on the reactivity of supramolecular complexes in zeolite catalysis	Salary for three years Postdoc (Dr. D. Lesthaeghe)

While some of these activities are complementary to my proposed programme of work, there will be no overlap in the use of funding. The ERC funding will be used to support additional members in my team - 1 post doc and 4 PhDs.

iii Early Achievement-Track-Record (max 2 pages)

My publication track record in international peer-reviewed journals is summarized in following table, in which the journals are ranked according to their impact factor.

Table 1 : Summarizing table of my publications (published and in press)

SCI index of journals (2000-2008)	ISI Impact (2007)	# published
Chemical Society Reviews	13.082	1
Angewandte Chemie - International Edition	10.031	3
Journal of the American Chemical Society	7.885	3
Chemistry - A European Journal	5.330	1
Chemical Communications	5.141	1
Organic Letters	4.802	1
Macromolecules	4.411	2
Journal of Chemical Theory and Computation	4.308	2
Journal of Physical Chemistry B	4.086	5
Journal of Physical Chemistry C	4.086	2
Journal with impact ≥ 4		21
Journals with impact >2		49
Journals with impact < 2		20
Total in ISI (20th October 2008)		84
Total in press		6

Various journals in which I published belong to the highest impact journals in the multi-disciplinary field of Chemistry (Angewandte Chemie – International Edition, Journal of the American chemical Society, Chemical Society Reviews, Chemical Communication, Chemistry- A European Journal). It is noteworthy that my first publication (Ab initio study of radical addition reactions : Addition of a primary ethylbenzene radical to ethene (I), V. Van Speybroeck, M. Waroquier, S. Wauters, M. Saeys, G.B. Marin, J. Phys.Chem.A, 2000, Vol. 104, 10939-10950 (SCI IF = 2.754)) in which a new model was presented to treat internal rotations in macromolecules, is already 68 times cited to date, indicating the significance of this research item. All subsequent papers on the internal rotor treatment received many citations. The software developed at that time is nowadays used by various international research labs.

I published 19 times as first author and published with more than 70 authors with various backgrounds going from experimentalists (e.g. Prof. Jim Haw, University of Southern California) to prominent theoreticians in the molecular modelling (e.g. Prof. Leo Radom, President of the WATOC (World Association of Theoretical and Computational Chemists)) and people from industry. I published with renowned scientists from various countries (Belgium, USA, Germany, Australia, Canada, Hungary, the Netherlands, Chile, Turkey, Singapore). For most of the papers I conceived the ideas, established the collaborations, implemented the new physical models and wrote the papers. I supervised the PhD students in their research work, wrote major parts of the papers, gave assistance and support in the analysis of the computational results and in many cases I performed the calculations by myself in order to keep under control the fast evolution of new developments in molecular modeling.

The number of citations to my publications is steadily growing (total citations in 2006 = 132, total citations in 2007 = 179, total citations in 2008 to date = 199) resulting to a global total of 648 citations.

Short description of selected publications :

- *Ab initio study of radical addition reactions: Addition of a primary ethylbenzene radical to ethene (I). Van Speybroeck V, Van Neck D, Waroquier M. Journal of Physical Chemistry A, 104 (46), 10939-10950, 2000, IF=2.765, Times Cited=68*
- *Why does the uncoupled hindered rotor model works well for the thermodynamics of n-alkanes ?, V.Van Speybroeck, P.Vansteenkiste, D.Van Neck and M.Waroquier, Chemical Physics Letters, Vol. 402, 479 - 484, 2005, IF=2.438, TC=22*

These two publications are representative for my work on internal rotations in macromolecules. The 2000 publication was my first paper where I presented a new model to treat conformational flexibility in macromolecules. This model development is particularly important for an accurate description of the preexponential factor for gas phase reactions. I have written new software, which is now used by many other laboratories over the world. The model presented there is referred as the 1D-HR model. The acronym 1D-HR model is now used by a large community and was first introduced in the Chem. Phys. Lett. publication.

- *An assessment of theoretical procedures for predicting the thermochemistry and kinetics of hydrogen-abstraction by methyl radical from benzene., Karen Hemelsoet, Damian Moran, Veronique Van Speybroeck, Michel Waroquier and Leo Radom, Journal of Physical Chemistry A, Vol. 110, 8942-8951, July 2006. IF=2.898, TC=18*

This work was initiated by various discussions I had with Prof. Leo Radom (School of Chemistry, Sydney, Australia and Chair of the WATOC, World Association of Theoretically Oriented Chemists) at several conferences (one of them WATOC2005 in Cape Town). As Prof. Radom is an expert in the determination of reaction barriers for a wide variety of chemical reactions, one of my PhD students has spent three months in Sydney to take up experience from his group. It has led to two common publications which received already many citations.

- *Understanding the failure of direct C-C coupling in the zeolite-catalyzed methanol-to-olefin process, David Lesthaeghe, Veronique Van Speybroeck, Guy B. Marin and Michel Waroquier, Angewandte Chemie - International Edition, Vol.45 (11), 1714 – 1719 (selected to be highlighted in the frontispiece), 2006, IF=10.031, TC=19.*
- *Zeolite shape-selectivity in the gem-methylation of aromatic hydrocarbons, David Lesthaeghe, Bart De Sterck, Guy B. Marin, Veronique Van Speybroeck and Michel Waroquier, Angewandte Chemie Int. Ed., 46 (8), 1311-1314, 2007, IF=10.031, Times Cited =5*
- *A complete catalytic cycle for supramolecular methanol-to-olefins conversion by linking theory with experiment, David M. McCann, David Lesthaeghe, Philip W. Kletnieks, Darryl R. Guenther, Miranda J. Hayman, Veronique Van Speybroeck, Michel Waroquier, James F. Haw, Angewandte Chemie – Int. Ed., 47 (28), 5179-5182, 2008, IF=10.031, Times Cited =0 (just appeared on the ISI)*

This work is an important breakthrough for my more recent work. Together with my PhD students that I supervise, we calculated reaction rates for a complex network (more than 100 reactions) occurring during the methanol-to-olefin (MTO) process over acidic zeolites. All our results were based on reaction rates instead of reaction barriers only. Over the past 30 years, the MTO process has been the subject of a vast number of studies from both industrial and academic researchers, leading to numerous controversies. We were the first ones to report reaction rates for this complicated network. All earlier results were based on reaction barriers only and never before the whole network were studied consistently. In this paper, a controversy of one of the most studies problems in catalysis was solved. This paper was the onset of very exiting research conducted in my group during the last two years. Our second Angewandte Chemie paper is based on results produced by one of my master students in 2006. According to the proposal of Prof. Jim Haw from the University of Southern California (J.F. Haw, D.M. Marcus, *Top. Catal.* 31, 41-48, 2005), we considered as actual catalyst the inorganic zeolite framework together with an organic hydrocarbon pool species that interact as a supramolecular catalyst. A theoretical study of the initial step alone has already provided us with new insights into shape selectivity. These major publications brought us in contact with Prof. Haw of the University of Southern California. I have spent there several short visits to discuss our theoretical results together with his experimental work. This cross-pollination between our two research groups resulted in a third Angewandte Chemie publication in which we reported for the first time a successful route for the MTO process that ties together experimental and theoretical results. Once more, our theoretical results are based on actual rate constants that take into account the full zeolite topology and were never done before. The publication has led to a cover picture of the Angewandte Chemie-International Edition Issue 47/2008 (http://molmod.ugent.be/cmm/wiki/Press_releases)

- *Insight into the solvation and isomerization of 3-halo-1-azaallylic anions from ab initio metadynamics calculations and NMR experiments., Reinout Declerck, Bart De Sterck, Toon Verstraelen, Guido Verniest, Sven Mangelinckx, Jan Jacobs, Norbert De Kimpe, Michel Waroquier and Veronique Van Speybroeck,* Chemistry – A European Journal, *in press, 2008. (IF=5.015)*In this work we calculated a quantum mechanical transition path for the isomerization of an important heterocyclic building compound. The most advanced molecular dynamics techniques to incorporate the full solvent effects were used. The calculations were performed by one of my PhD students. As corresponding author and last author I have written the entire paper. This work is a nice illustration of my latest interests to extend the techniques for the calculations of gas phase chemical kinetics to supramolecular systems.

I have given 15 talks on internationally established conferences. Very recently, I was invited by Prof. Leo Radom (President of the WATOC) to give an invited lecture at the WATOC2008 conference in Australia. The WATOC Congresses, which represent the major international conference on the computational chemistry calendar, take place only once every three years and so this is a very special opportunity to participate. (http://watoc2008.com)

Section 1b: Extended Synopsis of the project proposal (max 5 pages)

Situating the proposal & stating the aims:

The design of an optimal catalyst for a given process is at the heart of what chemists do, but is in many times more an art than a science. The quest for **molecular control** of any, either existing or new, production process is one of the great challenges nowadays.

Next generation catalytic materials should ideally have **a high selectivity** in combination with high yields for the desired process. However catalyst discovery heavily relies on serendipity, as the insight in the processes at the microscopic level is sometimes very limited. Any catalytic process is characterized by a complex network of reactions which hampers insight purely from experimental basis. Due to tremendous evolution of computational modeling during the last ten years, it may now be used as a **virtual microscope to study complex systems**. For simple reactions occurring in the gas phase methodologies to study the mechanisms and kinetics are well established, but the extension towards larger length scales is far from trivial. In particular the accurate determination of rate constants of individual reactions taking place in porous materials is not well-known. The final goal of this proposal is to **develop a set of models and protocols for the accurate determination of chemical kinetics in nanoporous materials**. As **a result new intriguing perspectives are opened on the long term for the catalysis community as they would have tools to predict experimental measured rates.** A predicted rate constant is generally accepted as accurate, if it predicts measured rates within at least an order of magnitude compared to benchmark values. Focus lies in this proposal on nanoporous materials as they possess unique properties for catalysis due to their high surface to volume ratio. For applications in catalysis, open penetrating pores are required. Moreover the field of nanoporous materials is currently exploding due to the discovery of mesoporous compounds, which impressed the community of zeolites and microporous phases by the huge gap in the dimensions of the pores. Even though zeolites already had a substantial impact on the economics and sustainability of products and processes in many sectors of industry, and despite the fact that already an extensive amount of papers has appeared on various aspects related to these microporous materials, **there is still to date no well defined procedure available to calculate kinetics of reactions in these materials.** The true bottleneck is the proper account of the topology. Many researchers have reported reaction barriers, but the extension towards rates that include also the entropic effects is not explored. The new generation of mesoporous materials, i.e. **Metal Organic Frameworks (MOFs)** which are subject of this proposal, have gained enormous interest lately both in academia and industry due to their promising properties for separation, catalysis,… However the number of theoretical papers discussing properties of these materials is still extremely limited. Various methodological issues need to be accommodated to reach the final goal of this proposal and I will go through these various issues in the ongoing of this proposal. However before doing so, I want to emphasize **the impact of the material's topology on the reaction rates** by highlighting a very recent theoretical study performed in my research group. I refer to one my recent publications *"Zeolite Shape-Selectivity in the gem-Methylation of Aromatic Hydrocarbons", Angew. Chem.-Int. Ed., 46 (8): 1311-1314 (2007)*).

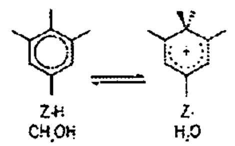

Figure 1 : Geminal methylation of aromatic hydrocarbons in zeolite materials

The model reaction is the gem-methylation of aromatic hydrocarbons that takes place in a series of industrial important zeolite materials (Figure 1). Industrially the reaction is carried out with alumino-phosphates that have the chabazite topology (HSAPO-34) and alumino-silicates with the MFI topology (HZSM-5). The chabazite topology has spacious cages that are interconnected by small windows, whereas the MFI topology has medium-pores. For academic purposes the beta zeolite is also often tested due to its large pore structure that allows direct introduction of large aromatic species into the material. Chemical kinetics reported in literature uses mostly very small clusters reducing the zeolite topology to very small fractions of the material (Figure 2A).

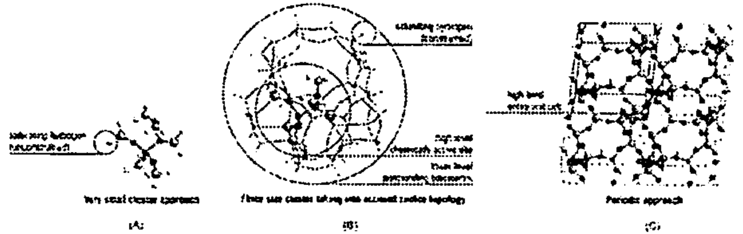

Figure 2 : Illustration of various methodologies to account for the zeolite topology

For this particular reaction given in Figure 1, the reaction rate varies over seven orders of magnitude in terms of the zeolite topology. This is illustrated in Figure 3 where the rates are given relative to the reference value obtained in a 5T cluster without taken into account the zeolite topology. The numbers reported here are probably the most reliable available in current literature, but still are obtained by making some drastic approximations. Several methodological developments are needed to accommodate for missing issues. In what follows I further elaborate on each of these missing links.

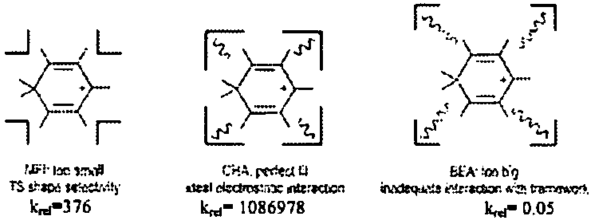

Figure 3 : Schematic representation of reactive intermediates in various zeolite topologies with varying pore size. k_{rel} is the relative rate for the geminal methylation reaction with respect to a small cluster model in which the zeolite topology is neglected.

Taking into account topology:

Following first principle methods are able to/ account for the topology of the nanoporous materials :

(i) Density functional theory or quantum mechanical methods are applied to a finite size cluster surrounding the active site. Eventually this high-level description of the active center is embedded into a classical electrostatic or force-field modelling of the surrounding framework (Figure 2B)

(ii) Periodic DFT approaches are performed on computational models consisting of one or more unit cells of the nanoporous material.

The pro's and the con's of both approaches are evident: periodic DFT calculations have the advantage that all factors depending on the structure of the nanoporous material (location of the active sites in the framework, shape of the pores and channels, flexibility of the porous material,..) are taken into account. On the contrary higher-level electronic correlation effects important for a correct description of Van-der-Waals interactions are not or almost not involved in DFT descriptions. The advent of new functionals can remedy to a large extent this issue but they should be thoroughly assessed (see further). Dispersion interactions are involved in high level quantum-mechanical approaches, but they can be applied only to clusters of modest size, and are hampered by problems related to convergence with respect to cluster-size and basis-set completeness.

Determination of rate constants from first principles :

The most applied method, due to its simplicity, to obtain the reaction rates from a microscopic viewpoint is **Transition State Theory (TST)**. Two ingredients are essential for the evaluation of the reaction rate: the reaction barrier and the preexponential factor determined from the molecular partition functions. They are obtained by use of static methods. However for reactions with a complex reaction coordinate (vide infra) static methods are mostly not adequate and molecular dynamics techniques are more appropriate.[3] Reactions that take place in the pores of a nanoporous material that is additionally loaded with solvent occur on a potential energy surface with various minima. In these cases direct sampling of phase space by means of molecular dynamics techniques is a viable alternative. It also takes into account anharmonic effects. The major drawback for these type of methods is that the probability of sampling the regions of phase space corresponding to a transition from reactants to products is in most cases very low due to the high energy passes that needs to be overcome.[4] A variety of techniques have already been proposed in literature to sample such rare events but in many cases these rely very heavily on a good choice for the reaction coordinate. The metadynamics method is a relatively new molecular dynamics technique that enables to enhance the sampling of separated regions of phase space and map out the underlying free energy landscape as a function of a small number of collective variables.[5] The proposed methodology is expected to be especially useful in these cases where complex and concerted transformations take place.

Methodological bottlenecks and solutions :

(i) **Dispersion interactions** : A first crucial issue to be tackled concerns the supramolecular nature of all investigated systems. Dispersion interactions including long-range attractive forces should definitely be taken into account. To date, only very advanced ab initio correlated wave-function methods are able to account for these effects. Unfortunately they are computationally too demanding for routine studies on large molecular systems (>50 atoms) under study in this proposal. DFT methods are the only potential alternatives, but a serious drawback is that most of all common density functionals can not describe long-range electrostatic correlations. The DFT problem for vdW interactions now has become a very active field of research and progress is

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[3] B. Ensing et al., Proc. Natl. Acad. Sci. (USA), 2005, 102, 6755.
[4] B. Ensing et al., Acc. Chem. Res., 2006, 39, 73.
[5] A. Laio et al., Proc. Natl. Acad. Sci. (USA), 2002, 99, 12562.

made on this issue. We mention in particular the work of Grimme with the so-called DFT-D approach. [6] We plan to implement it in the periodic codes which are commonly used in my research group (CPMD, CP2K and others[7]) and to assess this method :

(a) in some selected test reactions (vida infra) in zeotype materials, and in
(b) in MOFs studying the adsorption of xylene isomers and ethylbenzene with the microporous vanadium(IV) Terephthalate (MIL-47) (in collaboration with an external experimental partner (COK-KULeuven)[8]). The experimental results ascribe the different interaction energies of the guest molecules to molecular packing effects inside the sterically confining environment of the MIL-47 pore system. These experimental findings may serve as a stringent test for the DFT-D method suggested in this proposal, as the parallel orientation that was found for para-xylene is ascribed to strong pi-pi interactions. A theoretical explanation would be regarded as **ground breaking**.

(ii) Partially optimized structures: The borders of a finite cluster are fixed during the geometry optimization to prevent unphysical deformation that would result from the neglect of the molecular environment. The final optimized geometry does not correspond to an equilibrium structure leading to spurious frequencies that can not be used for the construction of the partition functions. Use of the Mobile Block Hessian (MBH) approach, developed by one of my PhD students is a valuable remedy [9]. The model is extremely useful to apply in porous materials having various layers of flexibility : (i) the chemically active part which is entirely free, (ii) the borders of the material which are very rigid (iii) the further content of the pores such as additional solvent molecules that might be treated as mobile blocks in the pores. It only requires some slight modification of the existing methodology.

(iii) construction of force field (FF): For computations nanoporous systems are commonly divided in various regions that are described by various levels of complexity ranging from very complex quantum mechanical approaches to classical force fields. Transferable force fields that can accurately describe the bulk zeolite structure and the interactions between solvent species and the surface area of the porous materials, are still not available. Recently, a completely new innovative methodology[10], i.e. the Gradient Curves Method (GCM), was proposed within my group. It differs from commonly known forcefields in the basic concept: no presupposed analytical expressions are introduced but the different terms figuring are generated on basis of the gradients resulting from a very extended and highly accurate training data set. Within the framework of this proposal we want to extend the original formulation of the force field to include longe range Van Der Waals and electrostatic interactions.

(iv) flexibility of the nanoporous materials. Nonoporous materials are often much more dynamic than generally believed. Experimentally it was observed that gas molecules larger than the smallest pore diameter in sodalite zeolite could diffuse through the narrow sodalite windows. The effect was attributed to the lattice flexibility of the zeolite. For the hybrid materials, drastic volume changes have been observed keeping the same topology due to strong host-guest

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[6] S. Grimme, J. Antony, T. Schwabe and C. Muck-Lichtenfield, Organic & Biomolecular Chemistry, 2007, 5, 741-758.

[7] http ://www.cpmd.org and http://cp2k.berlios.de/

[8] Prof. Dirk De Vos (Centre for Surface Chemistry and Catalysis, COK, KULeuven), with whom the CMM is involved in a project on "functionalized supramolecular systems

[9] A. Ghysels et al. "Normal modes in partially optimized systems", J. Chem. Phys.,2007,126(22), art.nr. 224102 ; A.Ghysels et al. "Calculating reaction rates with partial Hessians : validation of the MBH approach", J.Chem.Theory and Comp., 2008, Vol.4 (4), 614.

[10] T. Verstraelen, D. Van Neck, P.W. Ayers, V. Van Speybroeck, M. Waroquier, "The gradient curves method : An improved strategy for the derivation of molecular mechanics valence force fields from ab initio data", J.Chem. Theor. Comput.,Vol.3(4), 1420.

interactions. Cluster approaches are inherently not suitable to describe this effect, we have to shift to full periodic approaches in which the cell dimensions are taken up as additional variables during the calculation of the geometry and other derived quantities.

Rationale for chosen materials and applications :

Following nanoporous materials are considered within this proposal :

(a) **zeotype materials**, both alumino-silicates and alumino-phosphates containing micropores with various topologies (CHA, MFI, BETA, LEV, AFX). These materials are relevant for the methanol-to-olefin process (MTO). As this is a typical application in which the topology plays a crucial role, it is ideally suited to test the proposed methodological developments. The test reactions are inspired by recent unpublished work of my research group for which we encountered methodological deficiencies. The importance of long-range interactions will be evaluated for two reactions : methylations of aromatic compounds and ring contractions of polymethylbenzenes. For the first reaction the charge changes in going from the reactants to the transition state. For the second reaction the zeolite does at first sight not actively participate. Secondly, the same reactions will be evaluated on alumino-phosphates to evaluate the influence of composition on the reaction rates. Up to date, reaction rates in alumino-phosphates were never reported. These polar zeotype materials are more difficult to model : Small cluster suffer from unrealistic dipole moments. Reaction rates will be evaluated within a finite cluster and periodic model approach. This choice of reactions and materials enables us to discriminate between zeolite topology and composition effects on the reaction rates. Finally, the molecular dynamics approach will be used to obtain reaction rates of the ring contraction of heavily substituted aromatic rings. Preliminary results have indicated that the zeolite breathing can help in squeezing these intermediates towards smaller rings.

Previously carefully selected test reactions will enable to test each of the methodological aspects of the proposal. The MTO process is taken as a case study but serves as an ideal understanding of numerous aspects throughout heterogeneous catalysis.

(b) **Metal-Organic Frameworks (MOFs)** : In a first phase, the adsorption behavior os xylene related isomers will be studied MIL-47, MIL-53. These materials were found potential candidates for the effective separation of various aromatic related organic compounds [11,12]. For para-xylene the interaction with the MOF framework was limited compared to other xylene isomers. The correct description of these host/guest interactions are a stringent test for the DFT-D approach and for commonly used force fields. As a result of this research, we will be able to formulate a recipe for the calculations of accurate interaction energies in the hybrid materials. This research is the ideal step-stone towards the study of reactions in MOFs. Herefore the oxidation of toluene towards benzaldehyde is selected. The MIL-47, MIL-59 and MIL-61 materials will be tested for catalytic oxidation reactions by the COMOC Research Unit of our University. The centre which is leaded by Prof. Pascal Van der Voort has proven record in the synthesis and characterization of ordered porous materials. The latter materials are vanadium based MOFs and in order to compare their performance to existing materials also large-pore vanadium incorporated aluminophosphates (VAPO-5) will be studied [13]. For these materials in which transition metal ions are involved, we will need to take care of the spin-state of the transition metal ion and its influence on the chemical reactivity.

This part of the proposal has a very high level of risk. Although by optimal interaction with our experimental partner and by means of the large variety of possible methods outlined in the methodological section, theoretical predictions regarding the mechanism and rates of these reactions should be feasible.

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[11] L. Alberts et al. "Selective adsorption and separation of xylene isomers and ethylbenzene with the microporous Vanadium(IV) Terephthalate MIL-47, Angew. Chem. Int. Ed. 46/2007, 4293

[12] V.Finsy et al. "Pore-filling-dependent selectivity effects in the vapor phase separation of xylene isomers on the metal-organic framework MIL-47", JACS, 2008,Vol. 130, 7110

[13] In collaboration with COMOC - UGent

ERC Starting Grant

Research proposal (Part B2)[14]

Section 2: ***The Project proposal*** **(max 15 pages + Ethical Issues)**

i. State-of-the-art and objectives

Molecular modeling simulations are gradually becoming a ubiquitous tool in many fields of science and engineering. They may lie at the basis of the discovery of new phenomena and the elucidation of the physics that govern the behavior of novel systems. In cases where controlled laboratory experiments are too difficult or impossible, simulations can be used to construct virtual experiments for study of complex systems. Similarly, in situations where experimental results are ambiguous or indirect, simulations provide an ideal complement for precise interpretation of laboratory data. One particular challenge is the accurate determination reaction rates of chemical reactions starting from molecular ingredients. **The aim of this proposal is the first principle determination of chemical kinetics of reactions taking place in nanoporous solids,** which are particularly important for catalytic applications. The understanding of elementary reaction steps at the molecular level is crucial in the optimization of the catalyst, in order to obtain high selectivities, high yields and ideally also catalyst sustainability. The applications of this proposal are situated in the field of nanoporous materials that have a high surface to volume ratio and have very ordered, uniform pore structure. Due to their versatile and rich surface composition, surface properties; they are ideally suited for functional applications such as catalysis.
Despite the rapid evolution in computational chemistry and physics, there is no standard procedure available to determine reaction rates in these materials from first principles. A large amount of papers is available discussing on various mechanistic aspects of catalytic reactions in porous materials. Reaction barriers are nowadays frequently reported, although the proper inclusion of the material's topology is often neglected. The extension towards reaction rates in these materials that can directly be compared to experimental data is only reported in a few papers. Up to date the calculations are very often done by reducing the actual catalyst to only a very small molecular environment.

Following methods are able to account for the topology of the nanoporous materials in applications of first principle methods (Figure 1):

(iii) Density functional theory or quantum mechanical methods are applied to a finite size cluster surrounding the active site. Eventually this high-level description of the active centre is embedded into a classical electrostatic or force-field modelling of the surrounding framework

(iv) Periodic DFT approaches are performed on computational models consisting of one or more unit cells of the zeolite.

The pro's and the con's of both approaches are evident: While the evident advantage of periodic DFT calculations is that all factors depending on the structure of the nanoporous material (location of the active sites in the framework, shape of the pores and channels, flexibility of the porous material,..) are taken into account, higher-level electronic correlation effects important for a correct description of van-der-Waals interactions are excluded in DFT descriptions. Moreover calculation of molecular partition functions within a periodic DFT approach, have not been done so far. These properties are essential to account for the entropic contributions to the reaction rates. Cluster calculations have the advantage that also high level quantum-mechanical approaches can be applied, but only to clusters of modest size. Finite clusters that are large enough to accommodate the effects of topology are too large for correlated wave function

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[14] Instructions for completing Part B2 can be found in the Guide for Applicants on ERC Grant Schemes

methods. Another point related to the use of clusters is the fact that the borders are usually fixed during the geometry optimization to prevent unphysical deformations due to the neglect of the full material's environment. This has leads also to unrealistic predictions of the molecular partition functions.
For both cluster and periodic approaches, an often applied methodology is to describe part of the system with classical force-fields to keep computational expense feasible. The accuracy of the obtained rates, depends also on the adequacy of the used force-fields. For the materials which are subject of this proposal the availability of transferable force-fields is not well established.

Within this proposal various methodological issues that hampers today's straightforward calculation or reaction rates are tackled, by proposing appropriate physical models that might give a solution to these bottlenecks. On the long term, the outcome of this proposal will provide methodological procedures to calculate accurate rates in nanoporous materials.

Applications in two types of materials are studied in this proposal : (i) **zeotype materials**, both alumino-silicates and alumino-phosphates with various topologies that have industrial relevance (ii) **Metal Organic Frameworks**, a fairly new class of crystalline porous materials composed of organic and inorganic moieties which are linked by strong bonds. They are characterized by extraordinary surface areas and giant pores, which make them potential candidates for a whole set of applications in separation, catalysis,... Although catalysis, is potentially one of the most important applications of metal-organic porous materials, only a handful of examples have been reported.
The test reactions taken up in this proposal are inspired by collaborations with experimental partners working in the field of nanoporous materials, as the knowledge obtained both from theory and experiment are ideally combined to achieve insight in a cost-effective way.

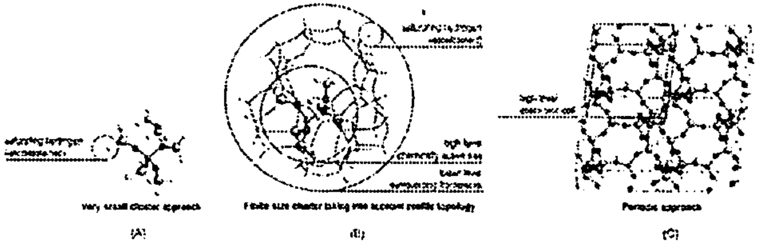

Figure 1 *: Illustration of various model spaces to account for the zeolite topology*

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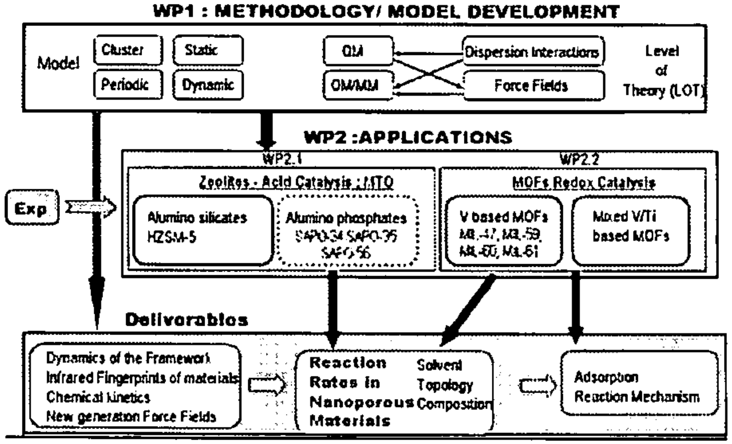
ii. Methodology
Before a molecule can react inside the pores of a material, it has to absorb and to diffuse to the active site. Diffusion will not be studied within this proposal; major emphasis is given to the determination of intrinsic reaction rates. For some specific materials adsorption will be studied as these properties may serve as benchmark for new proposed methodologies.



Scheme of workplan to persue in this proposal

METHODOLOGICAL BOTTLENECKS AND SOLUTIONS

REACTION RATES FROM STATIC AND DYNAMIC CALCULATIONS:

The most applied method, due to its simplicity, to obtain the reaction rates from a microscopic viewpoint is Transition State Theory (TST). Two ingredients that can be determined from the microscopic calculations determine the outcome of the reaction rate. The reaction barrier which is mainly determined by the electronic level of theory (LOT) and the molecular partition functions. The latter determine the result for the preexponential factor. For systems of relatively large scale, preference goes to Density Functional Theory based methods (DFT) for the reaction barrier, as they are very cost effective (cfr. Figure 2)
However for reactions with a complex reaction coordinate static methods are mostly not adequate. For this proposal, reactions that take place in the pores of a nanoporous material that is additionally loaded with solvent, is one of the reactions for which static methods fail. They fail because, it is not possible to point only one minimum for the reactants but instead various minima exist on the potential energy surface. In these cases direct sampling of phase space by means of molecular dynamics techniques is a viable alternative.[15] Direct sampling of the potential energy surface, also enables to account for anharmonic effects. The major drawback for these type of methods is that the probability of sampling the regions of phase space corresponding to a transition from reactants to products is in most cases very low due to the high energy passes that needs to be overcome. A variety of techniques have already been proposed in

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[15] B. Ensing et al., Proc. Natl. Acad. Sci. (USA), 2005, 102, 6755.

literature to sample such rare events but in many cases these rely very heavily on a good choice for the reaction coordinate.[16] The metadynamics method is a relatively new molecular dynamics technique that enables to enhance the sampling of separated regions of phase space and map out the underlying free energy landscape as a function of a small number of collective variables.[17]
The proposed methodology is expected to be especially useful in these cases where complex and concerted transformations take place.
For practical purposes, where the focus is on robustness and computational speed, the molecular dynamics based methods can not be taken as standard but for some well-defined reactions of this proposal, various advanced MD techniques will be tested and compared to the computationally more feasible transition state results.

ACCURATE TREATMENT OF LONG-RANGE INTERACTIONS

The target systems have a supramolecular nature. Supramolecular chemistry describes the chemistry beyond the molecule and studies chemical species held together by non-covalent intermolecular interactions. Such dispersion interactions are ubiquitous, long-range attractive forces which act between separated molecules even in the absence of charges or permanent electric moments. They stem from many-particle (electron-correlation) effects that are complicated by the quantum-mechanical wave-nature of matter. Only very advanced ab initio correlated wavefunction methods are able to account for these effects but are computationally too demanding for routine studies of the non-covalent interactions in larger (>50 atoms) chemically interesting systems. (cfr. Figure 2, illustrating computational feasible methods in terms of length and time scale). Density functional theory (DFT) is now the most widely used method for electronic structure calculations in condensed matter physics and quantum chemistry. This success mainly results from significant 'robustness', i.e. providing reasonable accurate predictions for many properties of various molecules and solids at affordable computational expense. However, a general drawback of all common density functionals is that they can not describe long-range electrostatic correlations that are responsible for the dispersion forces. The DFT problem for vdW interactions now has become a very active field of research and recently some proposals have been made. From a practical point of view, where the focus is on robustness and computational speed, empirical $-C_6R^{-6}$ corrections to standard density functionals seem most promising. This is called the DFT-D approach and provides high accuracy in many different situations[18]. To meet this goal we will be able to use some existing software such as CPMD and CP2K.[19] For the last program which has a very attractive scaling of computational time in terms of the number of involved atoms, additional program implementations need to be done to account for the extra van der Waals contribution. The program CP2K provides state-of-the-art methods for efficient and accurate atomistic simulations, sources are freely available and is therefore an ideal basis for new model implementations. The CMM is already part of the CP2K developer's team, as we contributed to the linear response part of the program in the presence of an external magnetic field.

KIG[20] 1 : Testing of Grimme Van der Waals parameters and recalibration of new parameters for the transition metals figuring in the MOFs

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[16] B. Ensing et al., Acc. Chem. Res., 2006, 39, 73.
[17] A. Laio et al., Proc. Natl. Acad. Sci. (USA), 2002, 99, 12562.
[18] S. Grimme, J. Antony, T. Schwabe and C. Muck-Lichtenfield, Organic & Biomolecular Chemistry, 2007, 5, 741-758.
[19] http ://www.cpmd.org and http://cp2k.berlios.de/
[20] KIG is defined as Key Intermediate Goal figuring in the Budget Table

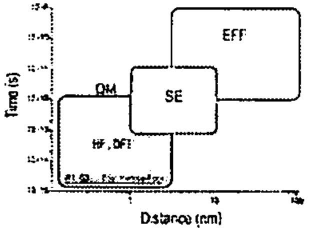

Figure 2 : Computational Chemistry Hierarchy. QM, SE, EFF, HF, DFT stand for quantum mechanical , semi-empirical, empirical force field, Hartree-Fock and Density Functional Theory methods, respectively.

A stringent test-case for the DFT-D method is the adsorption of xylene isomers on the microporous vanadium(IV) Terephthalate (MIL-47) material, which will be discussed thoroughly later in this proposal. The experimental results ascribe the different interaction energies of the guest molecules to molecular packing effects inside the sterically confining environment of the MIL-47 pore system. These experimental findings may serve as a stringent test for the DFT-D method suggested in this proposal, as the parallel orientation that was found for para-xylene is ascribed to strong pi-pi interactions. A theoretical explanation would be regarded as ground breaking.

KIG 2 : Development of Mobile Block methodology with various layers of flexibility

MOLECULAR PARTITION FUNCTION IN HO APPROXIMATION AND QM/MM CLUSTER APPROXIMATION.

As the number of atoms grows steadily in terms of larger pores, the full nanoporous material can not be treated at a full quantum mechanical level (cfr. Figure 2). The standard method to take into account part of the molecular environment in a computationally feasible way, uses an onion-like approach (Quantum Mechanics/ Molecular Mechanics : QM/MM). Various shells are introduced (Figure 1) that are treated to various levels of complexity, depending on their spatial extent from the chemical active part of the system. Within this procedure the border atoms are kept fixed to prevent unphysical deformations due to neglect of the full molecular environment. The latter assumption leads to highly unreliable partition functions, which cannot be used for the calculation of the preexponential factor. The problem can be circumvented by calculating the vibrational energy in the chemically active part of the system, only. Very recently the mobile block hessian (MBH) approach was introduced within my research group, which allows the calculation of partition functions for partially optimized systems[21]. Applications in porous materials have various layers of flexibility : (i) the chemically active part which is entirely free, (ii) the borders of the material which are very rigid (iii) the further content of the pores such as additional solvent molecules that might be treated as mobile blocks in the pores. Within this proposal, we want to extend the mobile block methodology to treat all layers with appropriate flexibility. This will give us accurate partition functions within a finite cluster model and within the harmonic oscillator approximation.

DETERMINATION OF ACCURATE, TRANSFERABLE FORCE FIELD FOR POROUS MATERIALS

The onion approach in the previous item, relies critically on the accuracy of the force field that is used to describe the zeolite-guest interactions. The latter should be able to describe properly

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[21] A. Ghysels et al., „Normal modes in partially optimized systems",J. Chem. Phys., 2007, 126 (22), Art. N° 224102; A. Ghysels et al. "Calculating reaction rates with partial Hessians: validation of the MBH approach", Journal of Chemical Theory and Computation, Vol. 4 (4), 614 – 625, 2008.

the bulk zeolite structure but also the properties between solvent species and the surface area of the porous materials. Such force field that has a high accuracy and transferability is not yet available. Recently, a new methodology , i.e. the Gradient Curves Method (GCM) was proposed within my group deriving accurate expressions for the classical potential. It does not postulate a priori analytical expressions for the various contributions to the force field but derives them on basis of the gradients resulting from a very extended and highly accurate training data set[22]. In the original description it was limited to valence interactions only, but recently it was also extended to long range Van Der Waals and electrostatic interactions, without introducing atomic charges a priori. This force field should be able to serve within the QM/MM methods.

KIG 3 : Development of an empirical model for the electrostatic interactions to determine non-bonding part of the force field.

KIG 4 : Parametrization of Van der Waals interactions based on a test set of high level ab initio calculations

KIG 5 : Determination of the valence parameters of the force field with the GCM method

ACCOUNTING FOR THE DYNAMICS OF THE FRAMEWORK AND BREATHING EFFECT.

Porous materials are often much more dynamic than generally believed. Experimentally it was observed that gas molecules with a diameter (Lennard-Jones diameter) larger than the smallest pore diameter in sodalite zeolite could diffuse through the narrow sodalite windows.[23] The effect was attributed to the lattice flexibility of the zeolite. Later on also theoretically this effect was observed by means of molecular dynamics simulations.[24] This breathing effect is more pronounced for the hybrid materials, studied within this proposal. This is schematically illustrated in figure 3 for the MIL-53 type of material, which may undergo shrinkage of the framework with drastic cell reductions of about 40 % and associated atomic displacements of about 5 to 3 Angstrom in various directions. These volume changes are heavily dependent on the molecules trapped in the pores of the material.

a: *as* b: *open* c: *hydrated*

Figure 3 : The different forms of MIL-53 (a) as synthesized; disordered terephtalic acid molecules lie within the tunnels; (b) high temperature (open); (c) room temperature hydrated form.[25]

This effect can no longer be described within a finite cluster approach with fixed borders and only a full periodic approach in which the cell dimensions are taken up as additional variables

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[22] T. Verstraelen et al., "The gradient curves method : An improved strategy for the derivation of molecular mechanics valence force fields from ab initio data", Journal of Chemical Theory and Computation, 2007, Vol. 3 (4) 1420 - 1434.

[23] R. M. Barrer et al., J. Phys. Chem. Solids, 1971, 32, 731-743.

[24] N. E. R. Zimmerman et al., J. Phys. Chem. C, 2007, 111, 17370-17381.

[25] K. Barthelet et al., Angew. Chem. Int. Ed., 2002, *41*, 281; K. Barthelet et al., Chem. Commun., 2004, 520.

during the calculation of the geometry is a viable methodology. To benchmark the accuracy of the periodic approach to determine flexibility of porous materials, we will first concentrate on a zeolite with MFI topology. Very recently, my research group succeeded in reproducing the MFO fingerprint in the infrared spectrum.[26] This observed band in the Infrared Spectrum at approximately 510-550 cm-1, is considered to be the spectroscopic signature of the MFI-type zeolite. Our findings were based on large cluster approaches in combination with in-house developed force fields. A stringent test of any periodic approach for the calculation of the vibrations is the reproduction of this typical MFI fingerprint. In a next step, the periodic approach will be applied for the calculation of the partition functions and reaction rates that are based on accurate frequencies that include also the framework vibrations.

KIG 6 : Benchmarking procedures for cell optimizations of zeotype and MOF materials

TEST REACTIONS AND APPLICATIONS

For the zeotype materials all test reactions are taking place during the Methanol-to-Olefin process - a promising alternative for the production of light olefins and which has been heavily debated over the past 30 years. It has been proven that the actual catalyst has a supramolecular nature, as illustrated in Figure 4, for which advanced theoretical techniques are of utmost importance.

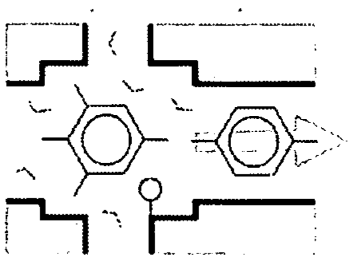
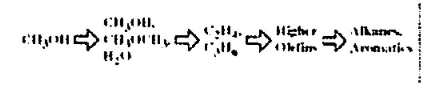


Figure 4: Schematic representation of the supramolecular catalyst within MTO.

REACTIONS IMPORTANT WITHIN THE METHANOL-TO-OLEFIN (MTO) PROCESS

Methanol to olefin (MTO) conversion on microporous zeolites is rapidly proving to be a case in heterogeneous catalysis where molecular-level concepts can be applied constructively.[27] As such, it is a very appropriate topic for exploring relationships between heterogeneous and homogeneous catalysis, and for further development of well-defined supported molecular catalysis. Figure 5 outlines in a general way, and with little mechanistic insight, the reactions of methanol on solid acids.[28]



$$CH_3OH \Rightarrow \begin{matrix} CH_3OH, \\ CH_3OCH_3, \\ H_2O \end{matrix} \Rightarrow \begin{matrix} C_2H_4, \\ C_3H_6 \end{matrix} \Rightarrow \begin{matrix} \text{Higher} \\ \text{Olefins} \end{matrix} \Rightarrow \begin{matrix} \text{Alkanes,} \\ \text{Aromatics} \end{matrix}$$

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[26] D. Lesthaeghe et al., J. Phys. Chem. C, 2008, 112 (25), 9186-9191.

[27] J.F. Haw and D.M. Marcus, in: Nanotechnology in Catalysis, eds. B. Zhou, S. Hermans, and G.A. Somorjai (Kluwer Academic Plenum, NY, 2004) ch. 13; J.F. Haw and D.M. Marcus, in: Handbook of Zeolite Science and Technology, eds. S.M. Auerbach, K.A. Carrado and P.K. Dutta (Marcel Dekker, NY, 2003) ch. 16.

[28] M. Stöcker, "Methanol-to-hydrocarbons : catalytic materials and their behavior", Microporous Mesoporous Mater. 29, 3-48 (1999); C.D. Chang, Catal. Rev. 25 (1983) 1.

Figure 5 : Conversion of methanol to hydrocarbons on solid acids

Methanol first equilibrates to a mixture containing water and dimethyl ether. A primary reaction, often following a kinetic induction period, then gives light olefins – largely ethene and propene. On solid acids of sufficient strength, secondary olefin reactions are also important. For example, propene may trimerize, and then crack into butenes and pentenes.

Since the demand of oil-based chemicals is rapidly increasing, the search for alternative natural sources is a highly topical subject. A crucial source of petrochemical feedstock will be provided by the conversion of methanol obtained from natural gas to light olefins catalyzed by acidic zeolites. In order to optimize the catalyst, i.e. control the ethene/propene ratio and to suppress secondary reactions that lead to coke formation, a detailed understanding of the reaction mechanism is indispensable. The last couple of decades, however, there has been tremendous dispute on the true nature of the reaction mechanism in MTO catalysis. During the last two years, my research team has provided strong theoretical proof for the failure of all direct mechanism[29] that were believed for almost thirty years. The results are in line with the recent experimental results proposing an alternative 'hydrocarbon pool' model, in which the active site of a typical MTO catalyst is proposed as a nm-size inorganic cage with an essential organic compound that interacts as a supramolecular catalyst[30].
Figure 6 shows compressed two-dimensional views of a catalyst particle during its lifetime. A typical crystallite is one to several hundred nm in diameter, and each cage is ca. 1nm. The catalyst bed has initially no activity because no cages contain aromatic rings. The kinetic induction period, characterized by very low methanol conversion, persists until sufficient methylbenzene sites form. Early in the lifetime of the catalyst, a few percent of the catalyst cages contain methylbenzenes and occasional methylnaphthalene. In middle age the catalyst crystallite has a larger number of both methylbenzene and methylnaphthalene sites and some cages have aged further and lost activity. Finally in a deactivated catalyst, as much as half of all cages contain polycyclic aromatic hydrocarbons and mass transport is severely restricted.

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[29] D. Lesthaeghe, V. Van Speybroeck, G.B. Marin, M. Waroquier "Understanding the failure of direct C-C coupling in the zeolite-catalyzed methanol-to-olefin process", Angew. Chem.-Int. Ed., 45, 1714-1719 (2006)

[30] J.F. Haw, D.M. Marcus, "Well-defined (supra)molecular structures in zeolite methanol-to-olefin catalysis" Top. Catal. 31, 41-48 (2005)

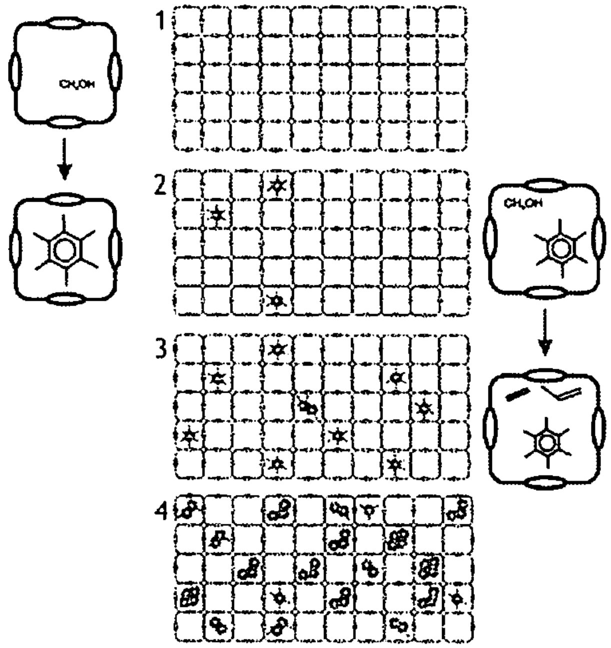

Figure 6 : Compressed, two-dimensional views of a catalyst particle during its lifetime.

Within the MTO process, my research team has performed ground-breaking theoretical work that resulted in three publications in Angewandte Chemie – International Edition :

- On basis of theoretical calculations on a complex reaction scheme consisting of more than 100 individual reactions, we were able to conclude that no single plausible route exists that directly leads from methanol to ethane. Thereby, we proved the failure of all direct mechanism[31] that were believed for almost thirty years.
- We have proven transition-state-shape selectivity for the initial step of the hydrocarbon pool proposal. [32] Geminal methylbenzenium ions form the main starting point from which commonly proposed HP routes (such as the "paring" and "side-chain" mechanisms) originate. [33] (Reaction M4 in Figure 7)
- This year, we reported a working catalytic cycle for the conversion of methanol to olefins, in full consistency with experimental and theoretical observations. This work resulted in a joint publication with the experimental group of Prof. Haw (University of Southern California) who performed pioneering work on the MTO process.[34]

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[31] D. Lesthaeghe et al., Angew. Chem.-Int. Ed., 2006, 45, 1714-1719.
[32] D. Lesthaeghe et al., Angew. Chem. Int. Ed., 2007, 46, 1311-1314.
[33] B. Arstad, J. B. Nicholas, J. F. Haw, J. Am. Chem. Soc. 2004, 126, 2991 – 3001.
[34] D. M. Mc Cann et al., Angew. Chem. Int. Ed., 2008, 47, 5179-5182.

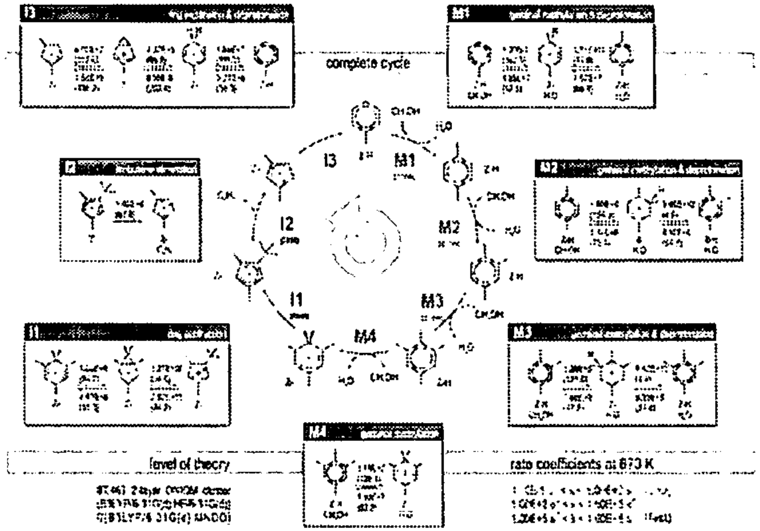

Figure 7 : Full catalytic cycle for carbon-carbon scrambling and isobutene formation from methanol through a combined methylbenzene/cyclopentenyl pool in HZSM-5. Calculated rate constants at 673 K are given in l/s and reaction barriers are 0K are given in kJ/mol. (taken from Angew. Chem. Int. Ed., 2008, 47, 5179-5182)

The rate constants reported in Figure 7, were obtained using the finite cluster QM/MM approach. Referring to my methodological section following contributions were neglected in the calculation of the rate constants:

- Long Range van der Waals energy contributions to the barriers
- Effect of loading of pores with additional solvent molecules
- Flexibility of the zeolite framework might not be accurately described within the finite cluster approach

For reactions M4 and I1 we will evaluate the importance of these missing links for the final results of the rate constant obtained within HZSM-5. The selection of reactions M4 and I1 is based on the following arguments:

- M1 is a reaction in which the charge changes from going to the reactants to transition state and the value of the reaction barrier is expected to be mainly controlled by electrostatic interactions, that are already taken up in the used DFT approaches
- For I1, ie. the ring contraction of polymethylbenzenes to smaller rings, the charge remains the same and the zeolite does not play an active role at first instance. In this case the effect of van der Waals contributions is expected more important.

KIG 7 : Calibrate a proper model to determine reaction rates is alumino-silicates and benchmark the theoretical results with experimental kinetic data for methylations of olefinic species.

KIG 8 : Determine reaction rates for methylations of aromatic species which account for long range interactions, loading with additional solvent species and flexibility of the framework in alumino-silicates

KIG 9 : Determine reaction rates for reactions in which the charge remains the same along the reaction path, taking into account long range interactions, loading with additional solvent species and flexibility of the framework in alumino-silicates

For the same reactions, the barriers and rate constants will also be determined in HSAPO-34, which is an alumino-phosphate zeotype materials. Historically, MTO catalysis has most often been performed on HZSM-5, but more recently the excellent performance of HSAPO-34 is rapidly gaining interest. Chemical kinetics in HSAPO-34 determined by theoretical techniques, have not been reported in literature. Defining an appropriate finite cluster model for alumino-phosphates, is much more difficult than for alumino-silicates due to the strong polar nature of the material. Small alumino-phosphate clusters are subject to unrealistic dipole moments created by the strong polarity of this material. We will define within the framework of this proposal an appropriate finite cluster model of considerable size that does not suffer anymore from the deficiencies of the smaller clusters. Every proposed model will be closely validated by spectroscopic data, obtained by our experimental partner (Prof. Haw) in this work from the USC. From preliminary but unpublished results performed in my team very recently, it might be anticipated that we will be able to define an appropriate cluster. Most probably adequate clusters will be very large (more than 300 atoms are needed to have realistic dipole interactions). In view of this, the periodic approach, which is much less prone to unrealistic dipole effects is also a viable alternative for the alumino-phosphates. It is the ideal example to test the applicability of the proposed periodic approaches in the methodological part for the calculations of the rates. Rates resulting from both finite cluster models and periodic approaches will be compared.
These proposed objectives are very ambitious, as nobody calculated kinetics in alumino-phosphates ever before and as rates from periodic calculations in zeotype materials were also never reported.

In addition previous reactions will also be calculated in various zeolite topologies. Following alumino-phosphates will be studied within this proposal: **SAPO-35, SAPO-34 and SAPO-56** with respectively, LEV, CHA and AFX topology. These topologies are selected since their cages are all interconnected by similar 8-ring windows but the cage dimensions vary by about 30%. These topologies will enable to discriminate between particular effects of zeolite topology effects on both reaction barrier and preexponential factor.

KIG 10 : Calibrate a proper model to determine reaction rates is SAPO-35, SAPO-34 and SAPO-56 and determine the reaction rates of methylations of aromatic species.

Finally, we will study the kinetics of geminal-methylations on heavily substituted aromatic rings, such as hexamethylbenzenium and heptamethylbenzenium ions. Recent unpublished research results have pointed out that these intermediates are severely restricted in space in the HZSM-5 topology. The breathing of the zeolite would additionally help to squeeze these intermediates to smaller rings.

KIG 11 : Determine reaction rates of geminal methylations of heavily substituted aromatic rings taking into account framework flexibility in restricted pore systems.

Previous carefully selected reactions in various zeotype materials, will enable to test each of the methodological issues outlined in the first part of the proposal. Following groundbreaking research results will be obtained :

1. Impact of dispersion interactions on electrostatically controlled and non-electrostatically controlled reactions
2. Quantitative comparison between rates resulting from periodic and finite cluster calculations
3. Quantitative comparison between rates resulting from static calculations and molecular dynamics calculations
4. Impact of zeolite breathing effect on the rate constant of industrially important reactions
5. Quantification of zeolite topology and composition effects on the reaction rates

This shows that the MTO process serves as an ideal step-stone to an increased understanding of numerous aspects throughout the field of heterogeneous catalysis.

MOFS

Before starting calculations on reactions taking place in MOFs, we will evaluate the accuracy of DFT and DFT-D methods for the description of accurate energies of guest molecules within these hybrid materials. A stringent test case to meet this goal concerns the **adsorption behaviour of xylene isomers and ethylbenzene within the microporous vanadium(IV) Terephthalate (MIL-47) material.** The choice for this application is motivated by a recent publication of the research group of Prof. Dirk De Vos, who is affiliated with the Centre for Surface Chemistry and Catalysis, COK, KULeuven. The CMM is already involved in a collaboration with the COK concerning a project on "functionalized supramolecular systems".
They reported for first time on the successful use of MOFs **as selective adsorbents for the extremely difficult and industrially relevant separations of para-xylene versus meta-xylene and para-xylene versus ethylbenzene.**

The one-dimensional pores of the isotypic materials MIL-53ht and MIL-47 are lined with terephthalate ligands and hydroxy or oxo groups which are connected by coordinatively saturated Al^{3+} , Cr^{3+} (MIL-53 ht), or V^{4+} ions (MIL-47).[35a,b]Both structures were fully characterized by
Férey and co-workers, who disclosed an impressive series of MOFs with new topologies.[21a-g]
MIL-53ht and MIL-47 show high thermal stability and have already been investigated as
adsorbents for H2, CO2, and CH4[21f,g] The lattice constants of MIL-47 undergo clear changes upon adsorption of thiophene, acetone, or aniline.[21h]

The experimental results report on average selectivities of 2.5:1 for the separation of para-xylene and meta-xylene, and 7.6:1 for the separation of para-xylene and ethylbenzene. The adsorbates were located inside the MIL-47 host, by Rietveld refinements of the X-ray powder diffraction patterns of MIL-47 sample, saturated by the various aromatic compounds. The major difference between the molecular arrangements of the three xylene isomers is the relative alignment of the aromatic planes of the molecules within a pair. For para-xylene, the benzene rings are almost perfectly parallel, with staggered methyl groups. This parallel orientation is indicative for a strong pi-pi interaction between the para-xylene molecules. The interaction of adsorbed para-xylene molecules with the terephthalate ligands in the pore walls is much weaker. The alignment in case of ortho-xylene is much less effective. In case of meta-xylene a less efficient packing is obtained compared with para-xylene due to unfavourable steric interactions. The

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[35] a) T. Loiseau, et al. , Chem. Eur. J. 2004, 10, 1373; b) K.Barthelet et al., Angew. Chem. 2002, 114, 291; Angew. Chem. Int. Ed. 2002, 41, 281 c) G. Férey et al., Science 2005, 309, 2040; d) S. Miller et al., Chem. Commun. 2005, 3850; e) K. Barthelet et al. , Chem. Commun. 2004, 520; f) G. Férey et al. Chem. Commun. 2003, 2976; g) S. Bourrelly et al., J. Am. Chem. Soc. 2005, 127, 13 519; h) X. Wang et al., Angew. Chem. 2006, 118, 6649; Angew. Chem. Int. Ed. 2006, 45, 6499.

observed selectivities in the liquid phase are not a consequence of different interaction energies between the MIL-47 framework and the adsorbed molecules, but result from molecular packing effects inside the sterically confining environment of the MIL-47 pore system.

This application will first serve as a stringent test for the DFT-D approach outlined in the methodogical section. The parallel orientation found for para-xylene was ascribed to strong pi-pi interactions, which is a prototypical interaction that can not be described by standard DFT methods.
For ethylbenzene the interaction with the terephthalate ligands was found much stronger and our theoretical calculations must be able to discriminate between the behaviour of the adsorbants.

KIG 12 : Simulating selective adsorption of xylene isomers in the microporous Vanadium(IV) Terephthalate MIL-47 pore system

The theoretical papers adsorption of guest molecules within MOFs were restricted to very small adsorbants (H_2 [36], C1 to C4 linear hydrocarbons [37]). The correct description of the experimental findings would be truly innovative.

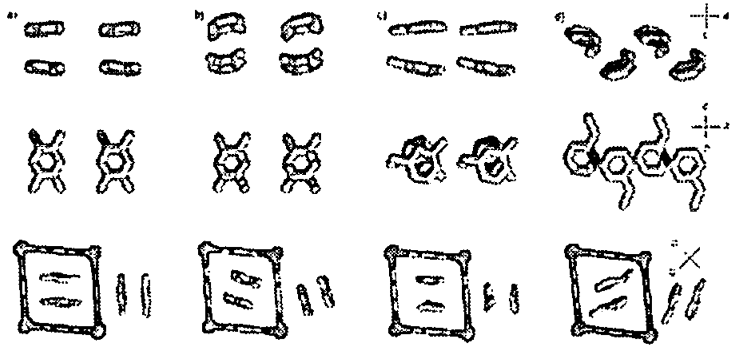

Figure 8 : Structure refinements of MIL-47 crystals loaded with different C8 alkylaromatic compounds: packing in the pores of a) para-xylene; b) ortho-xylene; c) meta-xylene;d) ethylbenzene (gray=carbon, red=oxygen, pink=vanadium; hydrogen atoms have been omitted for clarity). Figure taken from Angew. Chem. Int. Ed. 46/2007, 4293.

At second instance, the experimental results may be used to describe theoretically the breathing effect of the MOFs by periodic calculations in which the cell parameters and topology are taken up as additional variables in the geometry optimizations. A very recent paper by the research group of Férey, has investigated this breathing effect also from molecular simulations, that were

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[36] Han et al., J. Am. Chem. Soc., 2007, 129, 8422 - 8423

[37] Llewellyn et al., J. Am. Chem. Soc., 2008, 130 , 12808-12814

based on force fields. They used UFF force fields which are very general, but for which the accuracy to describe host/guest interactions for MOFs has not been validated. We will validate the appropriateness of various available force fields and benchmark them with the DFT-D results. If the available force fields are not sufficient, we will develop new ones based on the GCM methodology outlined in the first part of the proposal.

KIG 13 : Simulating breathing induced by various guest species in the MIL-53 pore system with the newly developed force field

The outcome of this part of the proposal will result in following innovative results :

1. The accuracy of DFT-D for the adsorption of aromatic-like molecules in MOFs
2. The accuracy of available force fields to describe host-guest interactions in MOFs
3. Next-generation force-fields with general applicability and transferability for other MOFs
4. Quantification of breathing effect in MOFs from molecular dynamics calculations with variable cell parameters.

These results form a crucial cornerstone for any future theoretical results on MOFs

A second phase in the applications related to the MOFs, concerns the calculations of reaction rates in these materials. Attention is focussed on the oxidation of toluene to benzaldehyde, shown in following figure 9. This reaction was selected because I have recently initiated a collaboration with the Centre for Ordered materials, organmetallics and catalysis (COMOC) research unit of our University. The centre which is leaded by Prof. Pascal Van der Voort has proven record in the synthesis and characterization of ordered porous support materials and heterogeneous catalysis. Recently a new PhD within this experimental group has started the research on the applicability of MOFs for these oxidation reactions.

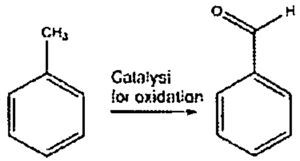

Figure 9 : Oxidation of toluene to benzaldehyde

Traditionally this reaction is performed in vanadium oxides (V_2O_5) but the selectivities and yields are restricted. Therefore metal-incorporated alumuniphosphate zeotype materials (VAPO-5 and VAPO-31) were already tested.[38] The obtained yields were still restricted to 60 or 70 %. and are interesting for their catalytic properties in various hydrocarbon conversion reactions. In particular, large-pore vanadium incorporated aluminophosphates (VAPO-5) is found to be active for the oxidation of aromatic compounds. However, recent results on the stability of VAPO materials in liquid-phase oxidation reactions are not so promising. Leaching of a small amount of vanadium into solution is observed. MOFs have already been suggested as possible alternatives as oxidation catalysts.[39] However as each MOF is a unique combination of cations and linkers, the chemical stability has to be investigated for each material.

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[38] Zahedi-Niaki et al., Applied Catalysis A, 2000, 196, 1, 9.

[39] L. Allaerts et al.; Chem. Comm., 2008, 1727-1737.

Within the framework of this proposal we will model the oxidation reactions and guide the experimentalist on basis of theoretically determined rate constants on plausible reaction mechanisms. In order to test various developed theoretical procedures following set of reactions will be studied. A first reaction is very simple but heavily debated, i.e. the gas phase oxidation of methanol towards formaldehyde. Although the reaction seems simple at first sight, it is heavily debated. It will enable to gain fundamental insight into different coordination of the metal ion in the MOF (completely saturated MOFS but also materials with one or two volatile ligands will be considered such as MIL-47, MIL-59 and MIL-61), different oxidation states and possible variations of linkers.

Next to the methanol oxidation that is discussed above, we will also study the liquid phase oxidation of toluene towards benzaldehydem compared to the gas phase oxidation of the same molecule. This reaction introduces liquid phase transport phenomena and solvent effects, but also introduces an aromatic system in the MOFs. Recent reports have shown that MOFs can be quite shape-selective for aromatic systems, not only due to sterical hindrance effects, but also to pi-pi stacking. We wish to explore this behaviour for the toluene oxidation reaction, using MOFs with different topology and different functionalities on the organic binders.

In case the vanadium based MOFs are not viable for the oxidation reaction, we might also validate on theoretical grounds the stability of mixed vanadium/titanium MOFs and their potential as active catalysts for the oxidation reactions.

KIG 14 : Theoretical study of gas phase oxidation reaction of methanol in Vanadium based MOFs. Elucidation of reaction mechanisms, catalytic active centers, determination of reaction rates.

KIG 15 : Theoretical study of gas phase oxidation reaction of toluene in Vanadium based MOFs. Elucidation of reaction mechanisms, catalytic active centers, determination of reaction rates.

KIG 16 : Theoretical study of liquid phase oxidation reaction of toluene in Vanadium based MOFs. Elucidation of reaction mechanisms, catalytic active centers, determination of reaction rates.

KIG 17 : Investigating potential new materials with a mixed Vanadium and Titanitum concentration and possible variation of linkers for the studied oxidation reactions

This part of the proposal has a very high level of risk. Although by optimal interaction with our experimental partner and by means of the large variety of possible methods outlined in the methodological section, theoretical predictions regarding the mechanism and rates of these reactions should be feasible.

iii. Resources (incl. project costs)

Existing resources contributing to the project : The infrastructure consisting of a series of high performance computers will still be available for my research team. The present team members of the CMM and especially the researchers working under my supervision must ensure transfer of knowledge of the established towards the new team.

Requested resources contributing to the project : The requested resources can be subdivided in three categories : personnel, operating costs and equipment. The most significant cost is the recruitment of high-qualitative researchers. The personnel cost includes funding for three PhD students and one postdoc which must allow pursuing the proposed research program. One PhD student starts from the onset of the research program to tackle the most critical issues of the proposal which have impact on the other activities. Such critical acitivity is the implementation of appropriate long-range interaction models in currently available software. The second year another two PhD students will join the research team and the planned research activities must reach full capacity. Preferably they have a different background allowing physical and chemical impulses into the various topics of the proposal. The requested budget foresees one senior researcher for the full period of the proposal. Potential candidates are more experienced postdocs who have defended their PhD thesis recently. There will be an international call guaranteeing some open competition for the most suitable candidate. The hosting of young postdocs from collaborating groups worldwide ensures a drain of knowledge towards the new team. In view of the intensive international collaborations I have built in the area of the porous materials, the new postdoc(s) should be willing to do short and midterm visits to the collaborative partners. In view of the advanced topics to be tackled with high risk potential, a postdoctoral fellow will substantially contribute to the success of the research activities.
For the recruitment of PhD students, I also plan to train promising young scientists who just obtained their master thesis. As I lecture several Master Courses which are closely related to my research field, I am quite well placed to attract potential physical and chemical engineers. In the past I was successful in convincing various students to perform their Master thesis within my group.

Sufficient budget should be reserved for operating costs. Per year additional budget is foreseen to cover all costs : conference fees and travel expenses for the attendance to conferences, short stays in external research groups, publication costs, small consumables..

At the start of the project also an equipment cost is included to buy a series of high performance workstations. This resource must guarantee an autonomous policy of the new team independent of the established team. Additional infrastructure needed to persue the research program will be used of the host institution. Although I will be able to access the current workstations of the Center for Molecular Modeling, the extra investments are crucial to pursue the research program. The planned applications are located near the limits of what is currently feasible considering computer power and method development. The research output of every individual researcher is critically dependent on their access towards high performance computer power.

iii. Budget - Table 1

Costs Category	month 1 to 18	month 19 to 36	month 37 to 54	month 55 to 60	TOTAL
Personnel	155,000.00	272,500.00	252,500.00	57,500.00	737,500.00
Subcontracting					0.00
Equipment	150,000.00				150,000.00
Consumables	3,418.33	3,415.00	3,000.00	1,000.00	10,833.33
Travel	15,000.00	15,000.00	15,000.00	5,000.00	50,000.00
Publications	3,000.00	3,000.00	3,000.00	1,000.00	10,000.00
Sub-total Other Directs Costs	171,418.33	21,415.00	21,000.00	7,000.00	220,833.33
Overheads	65,283.67	58,783.00	54,700.00	12,900.00	191,666.67
TOTAL	391,702.00	352,698.00	328,200.00	77,400.00	1,150,000.00

Addition of key interm. goal or milestone

iii. Budget - Table 2

„key intermediate goal", as defined in section 2.II.	Estimated % of total requested grant	Expected to be completed on month :	Comment
KIG 1	8%	36	
KIG 2	4%	12	
KIG 3	8%	24	
KIG 4	4%	48	
KIG 5	8%	48	
KIG 6	4%	18	
KIG 7	4%	24	

KIG 8	8%	36	
KIG 9	8%	36	
KIG 10	8%	30	
KIG 11	4%	48	
KIG 12	4%	18	
KIG 13	4%	54	
KIG 14	4%	36	
KIG15	4%	48	
KIG16	8%	60	
KIG17	8%	60	
Total	100%		

iv. Ethical Issues

(Note: Research involving activities marked with an asterisk * in the left column in the table below will be referred automatically to Ethical Review)

	Research on Human Embryo/ Foetus	YES	Page
*	Does the proposed research involve human Embryos?		
*	Does the proposed research involve human Foetal Tissues/ Cells?		
*	Does the proposed research involve human Embryonic Stem Cells (hESCs)?		
*	Does the proposed research on human Embryonic Stem Cells involve cells in culture?		
*	Does the proposed research on Human Embryonic Stem Cells involve the derivation of cells from Embryos?		
	I CONFIRM THAT NONE OF THE ABOVE ISSUES APPLY TO MY PROPOSAL	x	

	Research on Humans	YES	Page
*	Does the proposed research involve children?		
*	Does the proposed research involve patients?		
*	Does the proposed research involve persons not able to give consent?		
*	Does the proposed research involve adult healthy volunteers?		
	Does the proposed research involve Human genetic material?		
	Does the proposed research involve Human biological samples?		
	Does the proposed research involve Human data collection?		
	I CONFIRM THAT NONE OF THE ABOVE ISSUES APPLY TO MY PROPOSAL	x	

	Privacy	YES	Page
	Does the proposed research involve processing of genetic information or personal data (e.g. health, sexual lifestyle, ethnicity, political opinion, religious or philosophical conviction)?		
	Does the proposed research involve tracking the location or observation of people?		
	I CONFIRM THAT NONE OF THE ABOVE ISSUES APPLY TO MY PROPOSAL	x	

	Research on Animals	YES	Page
	Does the proposed research involve research on animals?		
	Are those animals transgenic small laboratory animals?		
	Are those animals transgenic farm animals?		
*	Are those animals non-human primates?		
	Are those animals cloned farm animals?		
	I CONFIRM THAT NONE OF THE ABOVE ISSUES APPLY TO MY PROPOSAL	x	

	Research Involving Developing Countries	YES	Page
	Does the proposed research involve the use of local resources (genetic, animal, plant, etc)?		
	Is the proposed research of benefit to local communities (e.g. capacity building, access to healthcare, education, etc)?		
	I CONFIRM THAT NONE OF THE ABOVE ISSUES APPLY TO MY PROPOSAL	x	

	Dual Use	YES	Page
	Research having direct military use		
	Research having the potential for terrorist abuse		
	I CONFIRM THAT NONE OF THE ABOVE ISSUES APPLY TO MY PROPOSAL	x	

Section 3: *Research Environment* (max 2 pages)

i. PI's Host institution

My host institution, the Ghent University (abbreviated to Ugent) is one of the major universities in the Dutch-speaking region of Belgium. More than 130 faculty departments, divided over 11 faculties, offer high-quality courses in every one of their scientific disciplines, each inspired by innovative research. Ghent University distinguishes itself as a socially committed and pluralistic university in a broad international perspective. After more than twenty years of uninterrupted growth, Ghent University is now one of the most important institutions of higher education and research in the Low Countries. Ghent University yearly attracts over 30.000 students, with a foreign student population of over 2.200 EU and non-EU citizens. Ghent University offers a broad range of study programs in all academic and scientific branches. With a view to cooperation in research and community service, numerous research groups, centres and institutes have been founded over the years.

Currently I am hosted within the Faculty of Engineering of the Ghent University and my research team is integrated within the Center for Molecular Modeling (http://molmod.ugent.be). I was co-founder of this research center, that was originally fully integrated within the faculty of Science. Since about a year, the time that I was appointed as Research Professor, I moved with part of my research team to the Faculty of Engineering. I was integrated in the education of physical and chemical engineers, my educational load was restricted to some courses in the Masters giving me the opportunity to have contacts with students at the most suitable moment that they have to choose the subject of their master thesis. Second argument was my personal interest in research where fundamental physical principles lie on the basis of very exciting applications in the engineering sciences.

The Center for Molecular Modeling (CMM) provided solid platform for undertaking my proposed programme of research. I see no reason why I should leave the Center of Molecular Modeling (CMM) in case the ERC starting grant would be awarded. In view of my current position at the Ghent University I have completely independent control of the accomplishment of my research projects. The CMM is currently composed of 20 researchers. It contains a theoretical division and a computational cell. There is a strong synergy between the various research cells stimulating cross-pollination. In addition the presence of physicists and chemists in the same Center is an ideal mixture to interchange ideas and to give mutual support. The interaction with competent theoreticians of the CMM gives an extra dimension to my research and was one of the ingredients that enabled me to go significantly beyond the state of the art. These researchers are very useful to bounce my ideas off and I intend to maintain this interaction on a regularly basis. This synergy has already proven to be highly successful in tackling a lot of scientific problems. It goes beyond the simple application of existing program packages.

Following intellectual interactions outside the CMM will stimulate the outcome of this research proposal

In the context of the submitted proposal two very recently set up collaborations will be intensified :

- A recently set up collaboration will be intensified with Prof. Dr. Pascal Van der Voort and relates to the synthesis of catalytic materials. He leads the Centre for Ordered materials, organmetallics and catalysis (COMOC) within the Faculty of Sciences. He joined the Ghent University only recently in 2006 and has proven record in the synthesis and characterization of ordered porous support materials and heterogeneous catalysis. This expertise in the designed synthesis of well defined porous materials is a new element for the Ghent University and is an opportunity for my research. An optimal interplay between his experimental research unit and my theoretical group, can lead to more efficient synthesis of new ordered porous materials. The prediction of the outcome of a chemical synthesis when large molecules are involved is very hard to predict from a purely experimental point of view. His research group has grown rapidly and now includes 4 PhD students, several undergraduates and 2 technicians.

- Another yet existing collaboration with the Centre for Surface Chemistry and Catalysis (COK) – KULeuven, will be intensified. The COK (with Prof.Dr.Pierre Jacobs as former head of the department) is a centre of excellence and is expert in the synthesis of microporous, mesoporous, nano-sized materials, two-dimensional solids, and supramolecular ensembles and membranes. The CMM is partner of the COK in the framework of the Interuniversity Attraction Poles (IAP -2007-2011) program "Functional Supramolecular System". The collaboration with Prof. Dirk De Vos, who is full professor at the KULeuven and leads a research team with following focal points of attention : zeolite catalysts, Layered Double Hydroxide Catalysts, Metal-Organic Frameworks as heterogeneous catalysts needs to be intensified. They recently reported on the selective use of MOFs as selective adsorbents for separations of xylene isomers (Angew. Chem. Int. Ed. 2007, 46, 4293). The further exploration of MOFs as alternatives for zeolites opens a new scientific horizon for the use of these unexplored materials on the long term.

Integration within a Materials Research Centre

Very recently the Faculty of Engineering has decided to launch a new centre of excellence on material research. It aims in physically grouping a large variety of research unities to create a pool of intellectual knowledge on material research. The intellectual challenge lies in bridging the gap from the molecular scale to the synthesis and testing of new materials for a large variety of applications. My research group has also been contacted to cooperate for the material research on the nanoscale. The ERC grant would allow me to fully cooperate in this initiative as independent researcher with an expanded clearly visible research group.

Access to existing computer infrastructure :

My research and in particular the numerical applications rely heavily on the availability of high performance computers. The Center For Molecular Modeling (CMM) has invested the last years intensively on a performing computer infrastructure and I will be able to access this computer park in the near future. However to guarantee my scientific independence, I will invest on new high performance computer units. This would guarantee an autonomous policy of my new established research team.

In addition the CMM has its own system administrator , so new research workers on the ERC project – if granted - can immediately start with their research. They will not be confronted with technical issues on the computer infrastructure.

The CMM has an administrative staff-member who arranges all administrative tasks for the financial management and personnel.

The new location will have no limit for hosting the new recruited staff of research workers.

ii. Additional institutions (additional participants)

VOLGENDE BIJLAGEN BIJ GRANT AGREEMENTS IN HET ZEVENDE KADERPROGRAMMA ZIJN STANDAARDDOCUMENTEN:

Annex II - General Conditions - the same for all projects under Co-operation/Capacities, modified for ERC and Marie Curie (which both offer Single or Multi-beneficiary versions).
Annex III - Unique to the following funding schemes to provide extra conditions on finance or reporting:

- SME actions
- Integrating Activities (Research Infrastructures)
- ERA-NET Plus
- Civil Society Organisation (CSO) actions

Annex V - Form B - Request for the accession of a new beneficiary to an existing Grant Agreement, e.g. for a grant which is already up and running.
Annex VI - Form C - Financial Statement per funding scheme - used to report costs claimed at the end of reporting periods.
Annex VII

- Form D - Terms of reference of the certificate on the financial statements (known as the Audit Certificate in FP6)
- Form E - Terms of reference for the certificate on the methodology (new to FP7) to be used for beneficiaries who want to get average personnel costs certified and/or for those who are unable to calculate real indirect costs and want to have a simplified method of calculating these certified.

Alle documenten zijn te raadplegen op
http://www.ukro.ac.uk/subscriber_services/fp7/participation/grant_agreements.htm.
of op
http://cordis.europa.eu/fp7/calls-grant-agreement_en.html

WO-Fiche

WBS-Element: B/10761/02 Fonds: IV2 Gecreëerd/gewijzigd door: Nathalie VANDEPITTE 09 264 30 29

Kredietcode: 41B03409 Begindatum: 01/01/2010 Datum: 21/09/2009
Kredietnaam: KINPOR Einddatum: 31/12/2014 Financieringsbron: 3712 BTW recuperatie
Kredietgever: EC Vakgroepnummer: TW17
Contractnummer: 240483 Titel: First principle chemical kinetics in nanoporous materials
Promotor: Prof. Veronique Van Speybroeck
Copromotor 1: Gekoppelde Kredietcodes:
Copromotor 2: WO-Fiche: origineel Gekoppelde WBS-elementen:
Copromotor 3: Versie: 1 Promotor:
Contractueel Overhead-regime: procentueel

CTRL+N = nieuwe versie WO-fiche **CTRL+S = kopie extern budget naar SAP**

Vak Administratie

05/406709

Budgetdrager.	EXTERN			INTERN			Toe te kennen budget	SAP	
	Netto-Budget (Excl. Overhead)	OH (contract)	Bedrag OH	Netto-Budget (Excl. Overhead)	OH (intern)	Bedrag OH	Budget	Budget	WBS-element
Person	737.500,00	20,00%	147.500,00	737.500,00	17,00%	125.375,00	762.072,65		
Recuperatie OH				24.572,65	17,00%	4.177,35			
2009	737.500,00		147.500,00	737.500,00		125.375,00	737.500,00	0,00	B/10761/02
2010	0,00			0,00				0,00	B/10761/02
2011	0,00			0,00				0,00	B/10761/02
2012	0,00			0,00				0,00	B/10761/02
2013	0,00			0,00				0,00	B/10761/02
2014	0,00			0,00				0,00	B/10761/02
Investering	150.000,00	20,00%	30.000,00	150.000,00	17,00%	25.500,00	150.000,00		
2009	150.000,00		30.000,00	150.000,00		25.500,00	150.000,00	0,00	B/10761/02
2010	0,00			0,00				0,00	B/10761/02
2011	0,00			0,00				0,00	B/10761/02
2012	0,00			0,00				0,00	B/10761/02
2013	0,00			0,00				0,00	B/10761/02
2014	0,00			0,00				0,00	B/10761/02
Werking	70.833,33	20,00%	14.166,67	70.833,33	17,00%	12.041,67	70.833,33		
2009	70.833,33		14.166,67	70.833,33		12.041,67	70.833,33	0,00	B/10761/02
2010	0,00			0,00				0,00	B/10761/02
2011	0,00			0,00				0,00	B/10761/02
2012	0,00			0,00				0,00	B/10761/02
2013	0,00			0,00				0,00	B/10761/02
2014	0,00			0,00				0,00	B/10761/02
	0,00	0,00%	0,00	0,00	0,00%	0,00	0,00		
2009	0,00			0,00				0,00	B/10761/02
2010	0,00			0,00				0,00	B/10761/02
2011	0,00			0,00				0,00	B/10761/02
2012	0,00			0,00				0,00	B/10761/02
2013	0,00			0,00				0,00	B/10761/02
2014	0,00			0,00				0,00	B/10761/02
	0,00	0,00%	0,00	0,00	0,00%	0,00	0,00		
2009	0,00			0,00				0,00	B/10761/02
2010	0,00			0,00				0,00	B/10761/02
2011	0,00			0,00				0,00	B/10761/02
2012	0,00			0,00				0,00	B/10761/02
2013	0,00			0,00				0,00	B/10761/02
2014	0,00			0,00				0,00	B/10761/02
Netto-inkomsten	958.333,33	20,000000%	191.668,67	982.905,98	17,000000%	167.094,02	982.905,98	Netto-inkomsten	Moeten de inkomsten ingegeven worden in SAP?
Overhead financier	191.666,67			167.094,02			167.094,02	OH in SAP	JA
Bruto-inkomsten	1.150.000,00			1.150.000,00			1.150.000,00	Bruto-inkomsten	

Gem. OH-% op te nemen in SAP

17,00%

Omzetting vreemde munt

=

www.tijd.be/koersen/index.asp?page=wisselkoersen&view=

Datum:

Brutobedrag	OH-Percentage	Nettobedrag	OH
0,00	0,00%	0,0000	0,0000
0,00	0,00%	0,0000	0,0000

OH (vast bedrag)	Brutobedrag	Nettobedrag	OH-Percentage
0,00	0,00	0,0000	
0,00	0,00	0,0000	0,0000%

B/10761/03 recup overhead 24572,65 EUR