

# EUROKIN

## 10<sup>th</sup> Anniversary Symposium

Eurokin is an industrial-academic consortium in the area of chemical reaction kinetics. Its aim is to transfer knowledge in reaction kinetics from the academic domain to the industrial domain, thereby expediting the implementation of the state-of-the-art. Financed by the industrial members, Eurokin achieves its goals by funding projects on various kinetics' topics using a mixture of experts drawn from its own academic members and the wider academic world as well as various consultants in the field. Founded in early 1998, Eurokin currently numbers nine industrial members (companies) and six academic members (European universities). You may find more information about the Eurokin consortium at <http://www.eurokin.org>.

To celebrate its 10<sup>th</sup> anniversary, a special symposium will be held at which experts in the field of reaction kinetics, who have previously hosted Eurokin projects, will return to make presentations in keynote areas of reaction kinetics relevant to the industrial world. The symposium is non-confidential and, unlike other Eurokin symposia, is open to both Eurokin and non-Eurokin members. The symposium will include a review of the work of Eurokin over the last decade by way of introduction. The details of the symposium are given below.

### Dates

The two-day meeting will be held on Monday and Tuesday 19-20 May 2008. (See schedule overleaf.)

### Venue

The venue of the symposium will be IFP-Lyon (France), a major centre for research and industrial development, for the oil, natural gas and automotive industries.

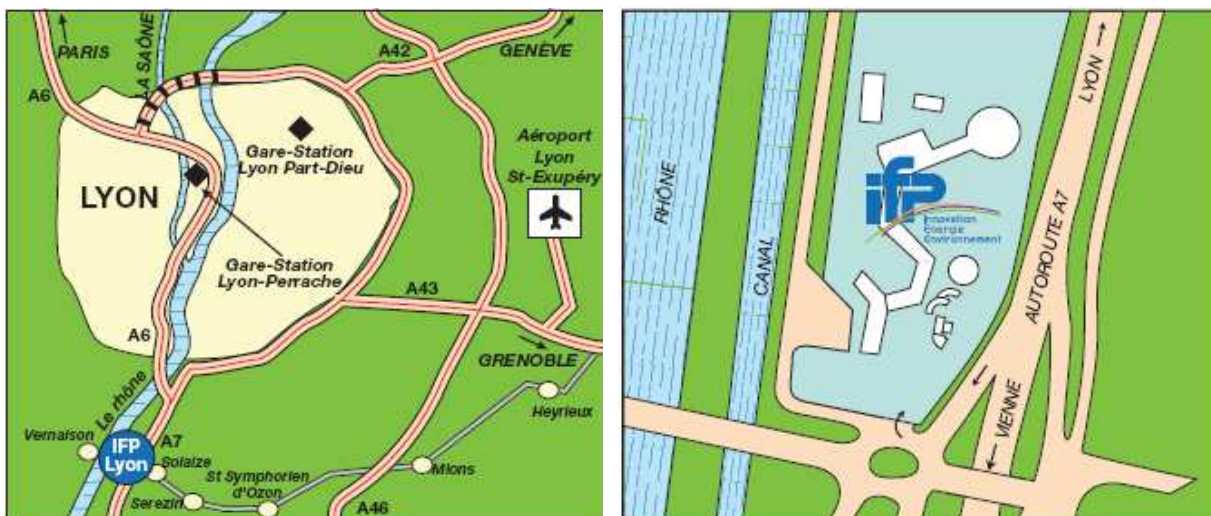


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Tel. : + 33 4 78 02 20 20;  
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## Location

Lyon is two hours from Paris by high-speed train (TGV). IFP-Lyon is about 15 km south of Lyon. To get to the conference with:

- Taxi or rental car: from Lyon to Solaize: take the A7 motorway south towards Vienne-Marseille, exit at Solaize, follow the sign 'Institut Français du Pétrole' (first right at the roundabout);
- From Lyon-Saint Exupéry Airport: take the A43 motorway towards Lyon, then the ring road ("boulevard périphérique") towards Marseille, then the A7 motorway.
- By train (SNCF): get-off at the Lyon Perrache station (best) or Lyon Part Dieu, then take a taxi.



## Registration

You are requested to register for this symposium by sending an email to Rob Berger ([Berger@anaproc.com](mailto:Berger@anaproc.com)). Since the numbers attending is limited, we recommend that you do this as soon as possible to guarantee participation. Following registration you will be notified of payment (vide infra).

## Registration fee

The registration fee is €185 per attendee for both days. The registration fee covers the symposium dinner and catering during the meeting and includes a subsidy by IFP.

## Poster

This symposium is an opportunity to meet colleagues and experts in the field of chemical reaction kinetics and we encourage you to make your own contribution in the form of a poster. Boards for displaying posters will be available around the conference room and can be viewed during the scheduled breaks.

## Open symposium

The Eurokin 10<sup>th</sup> Anniversary Symposium is open to both Eurokin members and non-members and therefore an excellent opportunity to meet colleagues and experts in the field of reaction kinetics. You are kindly requested to forward this invitation to colleagues within your own company or institution as well as to other contacts who might be interested in this symposium.

## Hotel accommodation

Pre-bookings have been made by IFP in the four hotels indicated in the table. Axotel, Berlioz and Charlemagne hotels are near Perrache Station in Lyon. Soleil et Jardin is outside the city of Lyon, near IFP. The IBIS and Kyriad hotel are already fully booked and are therefore not included in the table.

Hotel	night 18/19 May	night 19/20 May	night 20/21 May	Rate per night (€)	Address	Dead- line d)
<b>Axotel</b> <a href="mailto:axotel-perrache@hotel-lyon.fr">axotel-perrache@hotel-lyon.fr</a>	5	20	No rooms available	72 <sup>a)</sup>	12 rue Marc- Antoine Petit, 69002 Lyon. <a href="tel:+33472777072">+34 4 72 777072</a>	28 March
<b>Berlioz</b> <a href="mailto:reserv-hb@wanadoo.fr">reserv-hb@wanadoo.fr</a>	5	20	16	75/85/95 <sup>b)</sup>	12 cours Charlemagne, 69002 Lyon. <a href="tel:+33478423031">+33 4 78 423031</a>	27 March
<b>Charlemagne Best Western</b> <a href="mailto:charlemagne@hotel-lyon.fr">charlemagne@hotel-lyon.fr</a>	5	20	No rooms available	77/90 <sup>c)</sup>	23 cours Charlemagne, 69002 Lyon. <a href="tel:+33472777000">+33 4 72 777000</a>	27 March
<b>Soleil et Jardin</b> <a href="mailto:soleiletjardin@wanadoo.fr">soleiletjardin@wanadoo.fr</a>	5	10	10	110 <sup>a)</sup>	44 rue de la République, 69360 Solaize. <a href="tel:+33478024490">+33 4 78 024490</a>	26 March
<i>Total number of pre- booked rooms</i>	<i>20</i>	<i>70</i>	<i>26</i>			
a) Breakfast included.						
b) Breakfast € 8,-; single room rate / double room rate / triple comfortable room rate.						
c) Breakfast included; single room rate / double room rate.						
d) The following reference must be given to the hotel when booking: EUROKIN. The booking deadline is given for each hotel. After these deadlines, we cannot guarantee room availability. Booking accommodation and payment to the hotels are the responsibility of each participant.						

Additional information concerning the hotels and location of the symposium can be obtained from Mrs. Burlot-Ferré at IFP (e-mail: [Nadine.BURLLOT-FERRE@ifp.fr](mailto:Nadine.BURLLOT-FERRE@ifp.fr)).

Please make your booking before the deadlines given !

## Eurokin's 10<sup>th</sup> Anniversary Symposium: Programme

### Monday 19th May

- 10:30 - 12:00 *Visit of the IFP-Lyon centre (optional, please indicate your interest)*
- 12:00 - 13:30 Lunch
- 13:30 - 13:45 **Opening/Welcome**  
Hugh Stitt
- 13:45 - 14:45 **Introduction and demonstration of Eurokin tools**  
Rob Berger (Anaproc)
- 14:45 - 15:15 *Tea Break*
- 15:15 - 16:00 **Progress in catalyst deactivation**  
John Birtill (University of Glasgow)
- 16:00 - 16:45 **Creating and harnessing complex reaction networks: application to oxidation chemistry**  
Linda Broadbelt (Northwestern University)
- 16:45 - 17:30 **Progress in pollutant prediction in industrial combustion**  
André Nicolle (IFP)
- 19:30 Symposium Dinner

### Tuesday 20th May

- 9:15 - 10:00 **First principle chemical kinetics: from isolated molecules to supramolecular systems**  
Veronique van Speybroeck (Ghent University)
- 10:00 - 10:45 **Delivering scientific and business value with advanced modelling technology**  
Michael Caracotsios (UOP LLC and Northwestern University)
- 10:45 - 11:15 *Coffee Break*
- 11:15 - 12:00 **Title and speaker to be announced**
- 12:00 - 13:30 Lunch
- 13:30 - 14:15 **The use of CFD in chemical reactor analysis and design**  
Juray De Wilde (Université Catholique de Louvain)
- 14:15 - 15:00 **First principles kinetics of heterogeneously catalyzed reactions: oxidation of hydrocarbons over V<sub>2</sub>O<sub>5</sub> catalysts**  
Marie-Françoise Reyniers (Ghent University)
- 15:00 - 15:30 *Tea Break*
- 15:30 - 16:15 **Single-event microkinetic assisted design of new and improved catalytic materials**  
Joris Thybaut (Ghent University)
- 16:15 - 17:00 **Conductive Monolithic catalysts: Development and pilot tests for the industrial oxidation of o-xylene to phthalic anhydride**  
Enrico Tronconi (Politecnico di Milano)
- 17.00 Closure

## **Introduction and demonstration of Eurokin tools**

**Rob J. Berger**

Anaproc c/o TU Delft, Julianalaan 136, 2628 BL Delft, The Netherlands

The general aim of the Eurokin consortium is to produce a pre-competitive toolkit for estimating or measuring kinetic data and interpretation of those data by means of appropriate software routines. It will enable faster and lower cost derivation of kinetically based models, ultimately leading to more efficient commercial reactor design, quicker scale up and more efficient use of raw materials at lower costs.

The consortium was created in the spring of 1998 after an industrial survey in 1996 that revealed a need for improvement in kinetic research. The gathering of kinetic data was very costly and time consuming, and the software for parameter estimation from kinetic data was not user-friendly.

The Eurokin Consortium currently consists of 9 European (petro) chemical companies (Albemarle, BP, Dow, Eni, IFP, Johnson Matthey Catalysts, Linde, Shell, and StatoilHydro) and 6 academic centres (Delft Univ., Ghent Univ., UCL Louvain-la-Neuve, NTNU Trondheim, IRC-CNRS Villeurbanne, and Politecnico di Milano).

The Eurokin approach is to first gather knowledge about new subjects by means of reviews by experts in the field, followed by case studies to demonstrate the applicability and finally, if both previous steps were successful, develop suitable tools for the industrial research.

I will demonstrate a few tools that have been developed in the past ten years:

- (1) Selection sheet for a suitable method and test reactor for the kinetic experiments;
- (2) Spreadsheets to check for the absence of transport limitations and other phenomena causing non-ideality in the fixed-bed reactor and the slurry reactor;
- (3) Library of reactor models;
- (4) Some general recommendations for experimental kinetics research.

## **Progress in catalyst deactivation**

**John J. Birtill**

University of Glasgow, Scotland, UK

In this lecture I will briefly revisit some of the conclusions of the survey, which I completed in 2004, before moving on to consider some more recent developments. The focus will be mainly on measurement and modelling of deactivation kinetics. The content will include test methods for catalyst deactivation under normal conditions, accelerated decay, and also monitoring techniques for the working catalyst. Some examples of fitting simple models to test data will be examined, some unpublished work, others from the academic and patent literature, on processes such as dehydrogenation, hydrogenation, cracking, and oxidation of hydrocarbons. The insight into catalyst deactivation kinetics from some recent mechanistic studies will also be described. Finally, I will consider briefly some general approaches for minimizing catalyst deactivation.

## **Creating and Harnessing Complex Reaction Networks: Application to Oxidation Chemistry**

**Linda J. Broadbelt**

Department of Chemical and Biological Engineering, Northwestern University  
Evanston, IL 60208, USA

We have developed methods for automated generation of reaction mechanisms of complex systems that allow kinetic models of substantive detail to be built. Molecules are represented as graphs and matrices, and operations on these representations allow reaction to be carried out, molecule uniqueness to be determined, and properties to be calculated. We have applied our methodology to a wide range of different problems, including production of silicon nanoparticles, biochemical transformations, polymerization and depolymerization, and tropospheric ozone formation. While the chemistries we have studied are seemingly very disparate, applying a common methodology to study them reveals that there are many features of complex reaction networks that are ubiquitous.

This presentation will focus on two of the systems we have examined: lubricant oxidation, and tropospheric ozone formation. To gain insights into the degradation of lubricating oils, automated mechanism generation was used to study the condensed-phase oxidation of decane and octane. First, a library of structure-reactivity relationships was established that enables the estimation of all kinetic data required for solving large reaction mechanisms that model lubricant degradation. The development of this library of kinetic correlations relied heavily on high-level quantum chemical calculations, in which specific sub-families of the key reaction families were probed. It was shown that delineation of sub-families was critical to capturing the product selectivities and yields. Specific reaction rules are proposed that enable automated mechanism generation to be used, for the first time, to study condensed-phase free radical oxidation of large substrates. Models of decane oxidation were generated, and good agreement with available experimental data was achieved. The optimized parameters were then used to generate predictive models of octane autoxidation. Atmospheric chemistry involves a related set of oxidation reactions. Because of the diversity of the functional groups involved in tropospheric ozone formation, high-level quantum chemical calculations were applied to augment Benson's classic group additivity scheme, and a group additivity approach similar to the one used to estimate thermodynamic data was developed to estimate absorption cross sections over the wavelength region of tropospheric interest. Mechanisms were then generated automatically for various systems using different criteria for halting generation to control the explosive nature of the chemistry. A range of VOCs was investigated, including formaldehyde, acetaldehyde and acetaldehyde/alkane mixtures. The models were compared to experiments carried out at various NO<sub>x</sub> concentrations, and it was observed that the models were able to extrapolate well to different conditions.

## **Progress in Pollutant prediction in Industrial Combustion**

**Dr. Ir. André Nicolle**

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The prediction of pollutant formation and emission has become a major issue in the field of industrial combustion. Important pollutants include nitrogen oxides, sulfur oxides, unburnt hydrocarbons, volatile organic compounds, aromatic compounds and particulates. Besides their effect on health and environment, some pollutants may affect the overall combustion process as well as the evolution of each other. Pollutant formation is not only driven by chemical kinetics but also by its interaction with hydrodynamics and thermal transfer. A coupled approach is therefore preferable to purely chemical calculations in order to understand the impact of mixing and complex geometries on emissions.

In this presentation an overview of the existing methods used to predict pollutant formation as well as their strengths and weaknesses will be given. We will show how these methods can provide useful computational tools to design innovative pollutant control technologies. We will focus on the case of nitrogen compounds prediction. Recent works at IFP on the hydrodynamics - chemistry coupling will also be addressed.

**First principle chemical kinetics:  
From isolated molecules to supramolecular systems**

**Prof. Dr. ir. Veronique Van Speybroeck**  
Center for Molecular Modeling (CMM), Ghent University

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.

Of particular interest is the first principle determination of chemical kinetics for a variety of chemical reactions, going from isolated molecules to supramolecular systems, representing an aggregate of chemical species held together by non-covalent intermolecular interactions. All reactions in the field of homogeneous catalysis or more generally taking place in a solvent and reactions within the field of heterogeneous catalysis belong to the broad spectrum of applications.

To span the gap from the gas phase to extended molecular systems, a multiscale modeling approach is needed starting from simple structures (single molecules, molecular building blocks) and extending towards systems of growing complexity: polymer chains and supramolecular assemblies, systems embedded in a solvent, (macro) molecules adsorbed within porous materials.

Depending on the scale of the problem, state-of-the-art quantum chemical methods (QM) or empirical force-field (EFF) based molecular modeling techniques are feasible. Where QM methods are, in general, applicable to all chemical systems, regardless of connectivity, their computational expense makes them unfeasible for large (say, more than 200 atoms) systems. While state-of-the-art quantum mechanical methods are primarily suitable for single point or local energy minimizations, high-temperature molecular dynamics (MD) simulations are in a lot of cases too time-consuming. Nowadays due to some inventive theoretical algorithms ab initio molecular dynamics simulations are feasible for systems of a few hundred atoms.

In this talk an overview is given of a variety of theoretical models to predict the chemical kinetics of reactions occurring in extended systems. The most applied method to obtain the reaction rates from a microscopic viewpoint is Transition State Theory (TST). The accuracy of the results depends on the electronic level of theory (LOT) and the method used to construct the partition functions. The LOT is the determining factor for obtaining high accuracy for the activation energy and reaction enthalpy. For systems of relatively large scale, preference goes to Density Functional Theory based methods (DFT) as they are very cost effective. Although in principle for every new set of applications the most suitable level of theory should be validated by means of an extensive LOT investigation. The second kinetic parameter is given by the pre-exponential factor which is mainly determined by the partition functions. This issue gets much less attention in the literature. Within this talk an overview of developed

models and software within the CMM is given to determine accurate partition functions<sup>1,2</sup>.

For reactions occurring in an extended molecular environment, such as a solvent or a porous material, the standard TST approach can not be used. In a lot of cases, the border of the cluster is kept fixed, to prevent unphysical deformations that would result from the neglect of the full molecular environment. The introduction of constraints results in spurious negative eigenvalues in the frequency spectrum as part of the system was not optimized. Therefore, it is desirable to determine the vibrational energy in the chemically active part of the system, only. In 2002, Li and Jensen proposed the partial Hessian vibrational analysis (PHVA), in which a subblock of the Hessian is diagonalized to yield vibrational frequencies for partially optimized systems<sup>3</sup>. However this method assigns an infinite mass to the part of the system that was not optimized. It can be anticipated that this assumption works well for quite rigid systems but for reactions taking place in a solvent the aforementioned assumption might be too crude. Very recently we introduced the mobile block approach (MBA), that goes beyond the PHVA method, in which the non-optimized blocks still have a finite mass and can move as a rigid body with respect to the chemically active area. An overview of the MBA method and other extensions towards QM/MM methods will be given<sup>4</sup>.

All theoretical models will be illustrated by applications in a variety of fields including heterogeneous and homogeneous catalysis, polymerization, thermal cracking and coke formation and organic reactions taking place in solvents.

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<sup>1</sup> V. Van Speybroeck, M. Waroquier, S. Waueters, M. Saeys, G.B. Marin, "Ab initio study of radical addition reactions : Addition of a primary ethylbenzene radical to ethene (I), *J. Phys. Chem. A*, 104, 10939-10950 (2000).

<sup>2</sup> V. Van Speybroeck, P. Vansteenkiste, D. Van Neck, M. Waroquier, "Why does the uncoupled hindered rotor model work well for the thermodynamics of n-alkanes ?", *Chem. Phys. Lett.*, 402, 479-484 (2005)

<sup>3</sup> H. Li, J.H. Jensen, "Partial Hessian vibrational analysis : the localization of the molecular vibrational energy", *Theor. Chem. Acc.*, 107, 211-219 (2002).

<sup>4</sup> A. Ghysels, D. Van Neck, V. Van Speybroeck, T. Verstraelen, M. Waroquier, "Normal modes in partially optimized systems", *Journal of Chemical Physics*, 126, 224102, 2007.

## **Delivering Scientific and Business Value with Advanced Modeling Technology**

**Michael Caracotsios, Ph.D.**

Senior Associate, Process Modeling and Optimization, UOP LLC, 25 East Algonquin Road, Des Plaines, IL 60017, USA

Adjunct Professor of Chemical Engineering, Chemical and Biological Engineering Dept., Northwestern University, 2145 Sheridan Rd., Evanston, IL 60208, USA

It is not always clear how **Computational Technology** can deliver scientific or business value. In the academic environment and scientific journals quantitative analysis of experimental data or stand alone theoretical models are ubiquitous, whereas in the business environment searching for incremental value of computational technologies is a constant endeavor. In this seminar a narrow review of mathematical modeling technologies as applied to chemical and physical systems will be presented and some thoughts will be shared in creating value from these technologies.

The review will focus on mathematical modeling and sensitivity analysis of physicochemical systems. It will further address the quantitative analysis of experimental data with emphasis on parameter estimation, optimal experimental design, model discrimination and prediction under uncertainty. Finally a few thoughts will be shared on the subject of using linear and nonlinear optimization technologies to improve operations at the commercial level.

Thoughts in the area of creating value from modeling will focus first, on the subject of scaling models from laboratory to pilot plant to commercial operations, second on establishing the credibility of postulated models, but tuning to commercial data and finally on using, if appropriate, optimization methodologies to reduce operating costs or improve margins.

## **The use of CFD in chemical reactor analysis and design**

**Juray De Wilde**

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The design and scale up of chemical reactors is an important topic in the field of chemical engineering. It combines two essential elements: transport phenomena and chemical reactions. In industrial chemical reactors, mass and energy transport almost always affect the reactor performance (conversion, selectivity). It is essential to understand not only the chemistry and the transport phenomena, but also the coupling between them.

Computational Fluid Dynamics (CFD) has the potential of coupling chemistry and transport phenomena, rendering CFD particularly suited to obtain a more fundamental understanding of chemical reactors and to obtain data where experimental measurements are difficult. Furthermore, CFD offers promising means in validating traditional approaches and in progressing on problems for which traditional approaches fail.

An overview of the current status of reactor calculations combining CFD with chemical kinetics is given. The emphasis is on the emerging field of CFD in heterogeneous catalysis, involving multiple phases and, in many cases, multi-phase flow. Attention is paid to the barriers and limitations of CFD in reaction engineering and on the industrial impact of using CFD in reaction engineering.

**First principles kinetics of heterogeneously catalyzed reactions:  
oxidation of hydrocarbons over V<sub>2</sub>O<sub>5</sub> catalysts**

**Konstantinos Alexopoulos, Marie-Françoise Reyniers, Guy B. Marin**

(Ghent University, Laboratory for Chemical Technology  
Krijgslaan 281, S5, B-9000 Gent, Belgium)

Transition metal oxides are widely used as catalysts for the oxidation of hydrocarbons. Especially vanadium oxide based catalysts are among the most active for the oxidation of both aliphatic and aromatic hydrocarbons. An important example of such a catalyst is V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> (anatase), which is used in industry as an effective catalyst for the production of phthalic anhydride from o-xylene. Earlier experimental studies indicate that this catalytic system is of high performance when it consists of a monolayer of V<sub>2</sub>O<sub>5</sub> upon a TiO<sub>2</sub> (anatase) substrate, showing activity and selectivity not observed in the unsupported V<sub>2</sub>O<sub>5</sub> or TiO<sub>2</sub> anatase [1, 2]. This modification of the catalytic performance can be attributed to a synergetic effect between the active phase and the support. Nevertheless, mechanistic details of surface reactions and important elementary steps such as the initial hydrocarbon activation remain to be elucidated. Ab initio methods can help to obtain a quantitative insight in the activation mechanism and to unravel the role of the support on such a monolayer catalyst, thus providing a step towards a better understanding of the relation between structure and reactivity.

In this study the allylic C-H and the C=C bond activation of propene on fully oxidized vanadia surfaces are analyzed using density functional theory (DFT). Although the catalyst can be represented either as clusters cut out of the catalyst's surface with the dangling bonds at the cluster periphery saturated by hydrogen atoms or as periodic slabs [3], the necessity of considering spin polarization during the interaction of the hydrocarbon with the surface makes the use of the latter models more appropriate. Due to the finite size of the cluster models, the long range electron delocalization is largely suppressed and localized artifacts can occur when considering spin polarization in such cases. For the construction of the possible competing activation pathways all structurally and electronically distinct oxygen sites, i.e. singly coordinated vanadyl, doubly coordinated bridge and triply coordinated chain oxygen, of the catalyst have been taken into account. As hydrocarbon activation is affected by the structural and electronic properties of the catalytic surface, three experimentally relevant catalyst models have been envisaged, i.e. the unsupported vanadia catalyst represented by the (001) V<sub>2</sub>O<sub>5</sub> surface, the supported vanadia catalyst modeled by an epitaxial monolayer of vanadia on (001) TiO<sub>2</sub> anatase [4], and the unsupported vanadia catalyst where a lattice oxygen has been replaced by an oxygen molecule yielding less nucleophilic active sites [5].

For the allylic C-H bond activation two dominant reaction mechanisms have been found, with the vanadyl lattice oxygen being slightly a more reactive site. The use of a vanadia monolayer supported on titania strongly enhances the C-H bond activation as compared to bulk V<sub>2</sub>O<sub>5</sub>. On the other hand, the C=C bond activation

is favored in the presence of an electrophilic oxygen site resulting from the dissociative adsorption of molecular oxygen on an oxygen vacancy.

- [1] G.C. Bond, *Appl.Catal.A*, 157 (1997) 91
- [2] B. Grzybowska, *Top.Catal.*, 11/12 (2000) 23
- [3] M. Witko, *Catal.Today*, 32 (1996) 89
- [4] W. Gao, C.M. Wang, H.Q. Wang, V.E. Henrich and E.I. Altman, *Surf. Sci.*, 559 (2004) 201
- [5] R. Tokarz-Sobieraj, M. Witko and R. Grybos, *Catal. Today*, 99 (2005) 241

## **Single-Event Microkinetic Assisted Design of New and Improved Catalytic Materials**

**Joris W. Thybaut\* and Guy B. Marin**

Laboratory for Chemical Technology, Ghent University, Krijgslaan 281 S5, Ghent, Belgium [Joris.Thybaut@UGent.be](mailto:Joris.Thybaut@UGent.be)

The Laboratory for Chemical Technology at Ghent University has developed and applied the so-called Single-Event MicroKinetic (SEMK) methodology which maximally exploits the feature that the elementary steps in a complex reaction mechanism can be classified into a limited number of reaction families. Within such a reaction family unique rate coefficients can be identified, provided that symmetry considerations are appropriately accounted for. SEMK has been mainly applied to acid catalyzed reactions involving "free" carbenium ion intermediates (Martens and Marin, 2001; Narasimhan et al., 2004), but the feasibility of the methodology for radical processes such as thermal cracking and metal catalyzed processes such as Fischer Tropsch synthesis (Lozano et al., ) and aromatic hydrogenation has been demonstrated.

Next to the kinetic parameters, the incorporation of catalyst descriptors accounting for surface-sorbate interaction and other catalyst properties such as the total active site concentration, allows using a single SEMK model for an entire family of catalysts. Kinetic models featuring catalyst descriptors allow the development of better catalysts provided the former can be related to the catalyst composition and synthesis (Thybaut et al., 2006). High-throughput kinetic tests on series of catalysts over a wide range of reaction conditions provide libraries consisting of kinetic parameters rather than of conversions and selectivities and, hence, constituting a real knowledge data base which will provide guidelines for further catalyst development (Caruthers et al., 2003).

Caruthers, J. M., Lauterbach, J. A., Thomson, K. T., Venkatasubramaniam, V., Snively, C. M., Bhan, A., Katare, S., and Oskarsdottir, G., *J. Catal.* 216 , 98- 109, 2003

Lozano-Blanco, G., Thybaut, J.W, Surla, K., Galtier, P., Marin, G.B., *Oil Gas Sci. Technol.* 61 489-496 (2006) SCI-IF: 0.27

Martens, G.G., Marin G.B., *AIChE J.* 47, 1607-1622, 2001

Narasimhan, C.S. Laxmi, Thybaut, J.W., Marin, G.B., Denayer, J.F., Baron, G.V., Martens, J.A., Jacobs, P.A, *Chem. Eng. Sci.*, 59, 4765-4772, 2004

Thybaut, J.W., Narasimhan, C.S.L., Marin, G.B., *Stud. Surf. Sci. Catal.*, 159, 55-60, 2006.

## **Conductive Monolithic catalysts: Development and pilot tests for the industrial oxidation of o-xylene to phthalic anhydride**

**G. Groppi<sup>1</sup>, E. Tronconi<sup>1</sup>, F. Cruzzolin<sup>2</sup>, C. Cortelli<sup>2</sup>, R. Leanza<sup>2</sup>, and S. Marsaud<sup>3</sup>**

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<sup>3</sup> Corning Europe Technology Center, 77210 Avon, France

The operation of industrial multitubular packed-bed reactors with external cooling for strongly exothermic selective oxidations is typically limited by radial heat transfer. There is potential for significant enhancement of radial heat transfer rates if the random packings of catalyst pellets are replaced by structured catalysts with highly conductive honeycomb supports. In the past this concept has been proposed on the basis of simulation studies, confirmed by heat transfer and reactive experiments at the lab scale, and claimed in patents: to our knowledge however no proof-of-concept at an industrial scale has been reported so far in the open literature. We present herein results from a campaign (1600 hours) of o-xylene oxidation runs in a single-tube pilot reactor (i.d. = 24.6 mm) loaded with 16 washcoated (V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub>) monolithic catalysts with Al honeycomb supports and operated at typical industrial conditions for PA (phthalic anhydride) production. The highly conductive monolithic supports afforded substantially reduced T-gradients in comparison with reference runs in the same pilot reactor loaded with conventional ring catalysts, the maximum T-difference with the salt bath being halved at the same hot spot temperature (440 °C) and the mean bed temperature being about 20 °C higher. Temperature gradients were still moderate at the highest o-xylene feed load (400 g/h at Q<sub>air</sub> = 4 Nm<sup>3</sup>/h), which represents an upper limit for modern industrial PA packed-bed reactors. The Al honeycomb catalysts were successfully unloaded at the end of the runs. Model-based analysis provided an estimate of the overall heat transfer coefficient of 415 W/m<sup>2</sup>/K, versus 210 W/m<sup>2</sup>/K for the ring packing. The strong enhancement (≈2x) of radial heat transfer rates associated with adoption of highly conductive monolith catalyst supports is thus herein demonstrated at a representative industrial scale for the first time. It can be exploited e.g. either to increase the o-xylene feed load above 100 g/Nm<sup>3</sup> (and the PA productivity accordingly) within a retrofitting strategy, or to design new reactors with larger tube diameters.