INSTITUT DE FRANCE
Académie des sciences

CONFÉRENCE DÉBAT

Mardi 8 mars 2016 à 14h30
Académie des sciences – Grande salle des séances
23 quai de Conti, 75006 Paris

« LA CATALYSE, SUCCÈS ET ENJEUX – UN HOMMAGE À YVES CHAUVIN »

Organisateurs : **Philippe SAUTET et Pierre BRAUNSTEIN**
Membres de l'Académie des sciences

14 h 30 Introduction

14 h 40 Ménage à trois : Single-atom Catalysis, Mass Spectrometry and Computational Chemistry
Helmut SCHWARZ, *Technische Universität, Berlin*

15 h 20 From knowledge to design and from design to application
Avelino CORMA, *Associé étranger de l'Académie des sciences, Instituto de Tecnología Química, Universitat Politècnica de València*

16 h 00 De la conception des catalyseurs à leurs applications industrielles en pétrochimie : exemples de réalisations et défis pour le futur
Hélène OLIVIER-BOURBIGOU, *Institut Français du Pétrole, Energies nouvelles, Solaize*

16 h 40 Discussion générale et conclusion

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MENAGE A TROIS : SINGLE-ATOM CATALYSIS, MASS SPECTROMETRY AND COMPUTATIONAL CHEMISTRY

Helmut SCHWARZ

Selected examples of gas-phase reactions will be presented which are of timely interest for the catalytic activation of small molecules. Due to the very nature of the experiments, detailed insight in the *active site* of catalysts is provided and – in combination with spectroscopic studies and computational chemistry – mechanistic aspects of as well as the elementary steps involved in the making and breaking of chemical bonds are revealed.[1]

Examples to be discussed include *inter alia*: (i) Metal-mediated carbon-carbon bond formation; (ii) low-temperature, catalytic oxidation of CO; or (iii) the coupling of NH_3 and CH_4 to produce HCN. Of particular importance are the reactions of "bare" metal-carbene complexes, when generated in the gas phase and exposed to thermal reactions under (near) single-collision conditions.[2] In addition to the well-known metathesis and cyclopropanation processes, they exhibit rather unique reactivities. For example, at room temperature the unligated $[AuCH_2]^+$ complex brings about efficient C–C coupling with methane to produce C_2H_x (x = 4, 6), or the couple $[TaCH_2]^+/CO_2$ gives rise to the generation of the acetic acid equivalent CH_2=C=O. Entirely unprecedented is the thermal carbon-atom extrusion from halobenzenes (X = F, Cl, Br, I) by $[MCH_2]^+$ (M = La, Hf, Ta, W, Re, and Os) and its coupling with the methylene ligand to deliver C_2H_2 and $[M(X)(C_5H_5)]^+$. Among the many noteworthy C–N bond forming processes, the formation of CH_3NH_2 from $[RhCH_2]^+/NH_3$, the generation of CH_2=NH_2^+ from $[MCH_2]^+/NH_3$ (M = Pt, Au), or the production of $[PtCH{=}NH_2]^+$ from $[PtCH_2]^+/NH_3$ are of particular interest. The latter species are likely to be involved as intermediates in the platinum-mediated, large-scale production of HCN from CH_4/NH_3 (DEGUSSA process). Co-operative effects at a molecular level will be illustrated in the coupling of CH_4 with NH_3 by the heteronuclear clusters $[MPt]^+$ (M = coinage metal): platinum is crucial for the activation of methane while the coinage metal M controls the branching ratio between the C–N bond forming step and unwanted soot formation.

It will be shown that mass-spectrometry based studies on 'isolated' reactive species provide an ideal arena for probing experimentally the energetics and kinetics of a chemical reaction in an unperturbed environment at a strictly molecular level, and thus enable the characterization of crucial intermediates that have previously not been within the reach of conventional condensed-phase techniques. Clearly, these investigations open the door to a widely uncharted territory of chemistry, a field in which "each atom counts.[1]

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[1] For recent references, see: (a) H. Schwarz, Angew. Chem., Int. Ed. ***2015****, 54, 10090; (b) H. Schwarz, Isr. J. Chem.****2014****, 54, 1413; c) M. Schlangen, H. Schwarz, Catal. Lett.* ***2012****, 142, 1265; (d) N. Dietl, M. Schlangen, H. Schwarz, Angew. Chem. Int. Ed.* ***2012****, 51, 5544; (e) H. Schwarz, Angew. Chem. Int. Ed.* ***2011****, 50, 10096; (f) D. K. Bohme, H. Schwarz, Angew. Chem. Int. Ed.* ***2005****, 44, 2336.*

[2] S. Zhou, J. Li, M. Schlangen, H. Schwarz, Acc. Chem. Res. ***2016****, in press.*

FROM KNOWLEDGE TO DESIGN AND FROM DESIGN TO APPLICATION

Avelino CORMA

The design of a successful solid catalyst relies on the synthesis of materials with controlled adsorption and reactivity, to maximize selectivity towards the desired product. Thus, solid catalysts with well defined single or multiple sites have to be generated. We will show that this is possible by preparing structured inorganic micro- and meso-porous materials with controlled porosity and framework chemical compositions. Further possibilities can be envisaged by preparing structured hybrid organic-inorganic materials where the active sites can be introduced in the organic, the inorganic or in both the organic and inorganic moieties. This will allow the preparation of multifunctional solid catalysts for performing multistep reactions in a cascade manner. Then, it will be shown that the preparation of multifunctional catalysts can go beyond the lab and reach industrial application.

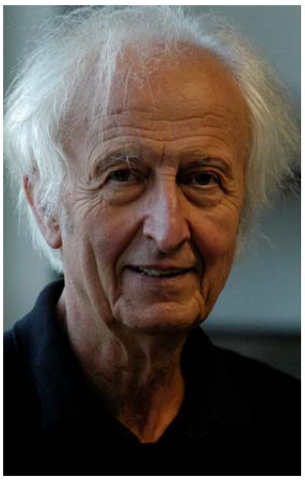
Finally, mono and bifunctional solid catalysts based on metal nanoclusters with a few atoms (3-10) and metal nanoparticles with controlled sizes and shapes within the range of 1 to 10 nm will be presented. With the metal nanoclusters entities, it is possible to achieve turnover frequencies close to those obtained by enzymes under very mild reaction conditions.

DE LA CONCEPTION DES CATALYSEURS A LEURS APPLICATIONS INDUSTRIELLES EN PETROCHIMIE : EXEMPLES DE REALISATIONS ET DEFIS POUR LE FUTUR

Hélène OLIVIER-BOURBIGOU

La catalyse homogène joue un rôle important dans le domaine de la pétrochimie. Pour cette industrie qui a besoin de réduire son impact environnemental et ses coûts, gagner en performances sur les catalyseurs est un levier de compétitivité. Pour répondre à ces enjeux de chimie durable, nous cherchons à concevoir de nouveaux systèmes catalytiques plus actifs et plus sélectifs, en intégrant dès leur conception, la technologie et le procédé de mise en œuvre. Faire avancer la science fondamentale tout en ne perdant pas de vue l'application industrielle est une démarche que nous menons depuis plusieurs années et qui est à l'origine d'un certain nombre d'innovations qui seront présentées. L'oligomérisation de l'éthylène en oléfines alpha-linéaires, utilisées pour l'industrie du polyéthylène, est un de ces exemples où l'adaptation de la structure du ligand à la nature du métal de transition et à son mode d'activation a permis d'établir des relations entre la structure des complexes et leur réactivité qui ont débouché vers des avancés clefs dans le domaine.

BIOGRAPHIES



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Helmut Schwarz studied chemistry at the Technische Universität Berlin (TUB) from 1966 – 1971. After completing his Ph.D. in 1972 under the supervision of Ferdinand Bohlmann and his Habilitation in 1974 (both at TUB), he spent some time abroad (ETH Zürich, MIT Cambridge, and Cambridge University) before in 1978 he returned to his *alma mater* to join the Institute of Chemistry. Dr. Schwarz has occupied visiting positions at 15 academic institutions worldwide, has delivered more than 1000 invited or name lectures and published > 950 peer-reviewed articles dealing with various aspects of gas-phase chemistry and physics. He has received close to 50 awards, distinctions, and honors from a dozen of countries. After having served from 2001 – 2007 as Vice President of the German Research Foundation (DFG), in January 2008 Dr. Schwarz was appointed President of the Alexander von Humboldt-Stiftung.

Avelino Corma earned his BS in Chemistry at Valencia University, PhD at Madrid under direction of Prof. Antonio Cortes, and spent two years postdoc at Queen´s University. He has been carrying out research in heterogeneous catalysis in academia and in collaboration with companies for nearly 30 years. He has worked on fundamental aspects of acid-base and redox catalysis with the aim of understanding the nature of the active sites, and reaction mechanisms. With these bases have developed catalysts that are being used commercially in several industrial processes. He is an internationally recognized expert in solid acid and bifunctional catalysts for oil refining, petrochemistry and chemical process, especially in the synthesis and application of zeolite catalysts. He has published more than 900 research papers, and inventor on more than 130 patents.

Corma has received numerous national and international prestigious awards and honors, including the F. Gault Award of the European Catalysis Society, the M. Boudart Award on Catalysis by the North American and European Catalysis Societies, the G. J. Somorjai ACS Award on Creative Catalysis, the National Award of Science and technology of Spain, "Rey Jaume I" Prize for New Technologies (2000), the ENI Award on Hydrocarbon Chemistry, the Royal Society of Chemistry Centenary Prize, Solvay Pierre-Gilles de Gennes Prize for Science and Industry, la Grande Médaille de l'Académie des sciences de France 2011, the Prince of Asturias Award for Science & Technology 2014, the 48th W. N. Lacey Lectureship in Chemical Engineering-Caltech (2015), the Jacobus van't Hoff Lecture 2015 at TU Delft Process Technology Institute, and the Hoyt C. Hottel Lecture in Chemical Engineering at MIT Chemical Engineering Department (2015). He is “Doctor Honoris Causa” of Utrecht University (2006), UNED (2008), Technische Universität München (2008), Universidad Jaime I de Castellón (2008), Universidad de Valencia (2009), Bochum University (2010), Universidad de Alicante (2010), Ottawa University (2012), Delft Technological University (2013), Jilin University (China) (2013) and University of Bucarest (2014).

Hélène OLIVIER-BOURBIGOU a effectué ses études à l'Université de Rennes (1984-85), obtenu le diplôme de l'Ecole Nationale Supérieure Pétrole et Moteurs (1985-86), puis effectué son doctorat en chimie à l'Université Paris VI, sous la direction du Prof. H. Kagan et de Y. Chauvin (1985-88). Elle a ensuite effectué un stage post-doctoral à l'Université du Sussex (Brighton) chez le Professeur M. F. Lappert (1989). Elle a soutenu son Habilitation à diriger des recherches à l'Université Paris VI (2005).

Depuis 1989, elle travaille à l'IFP Energies nouvelles, d'abord comme chercheur au Laboratoire de catalyse homogène (1989-1998), puis comme Project Manager (recherche industrielle et fondamentale) (1998-2003) et est responsable du Département de catalyse moléculaire depuis 2002. Ses principaux centres d'intérêts et réalisations scientifiques portent sur les applications de la catalyse homogène dans le secteur chimique, l'oligomérisation sélective des oléfines, les réactions de métathèse, la catalyse biphasique dans les liquides ioniques, la transformation des ressources renouvelables en bio-produits.

Elle a publié plus de 95 articles, dont 7 revues et 16 chapitres de livres et plus de 95 brevets. Elle est co-éditeur du livre « Multiphase Homogeneous Catalysis » (Wiley-VCH, 2004).

Elle a reçu le Prix Irène Joliot Curie « Femme scientifique de l'année » en 2014, le prix Montgolfier de la « Société d'Encouragement pour l'Industrie Nationale » en 1999 et le prix de la Division de catalyse de la Société Chimique de France en 1997.