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Tribute/Hommage

# A tribute to Edmond Payen: A singular vision between academia and industry

Edmond Payen (Figs. 1 and 2) was born in 1948 in Jenlain, a small village in the north of France that is well known for its beer. He graduated from the University of Lille – Sciences and Techniques. His PhD, which he defended in 1975, dealt with *"Synthesis, Raman and Infrared spectroscopic studies, of halogenophosphoric acids and pyrophosphoric halides"*. In 1983, he finally obtained his doctorate in Physical Sciences ("Habilitation"), which at that time corresponded to the highest university degree in France. The topic was related to Raman spectroscopy and the characterization of hydrotreating catalysts. It is also worth noting that Edmond had also graduated from the "Institut d'administration des entreprises" in Lille in 1973.

His own experience in academic research started in 1971 at the "Laboratoire de spectrochimie infrarouge et Raman" (LASIR) during his PhD thesis. After having accomplished his military obligation, he obtained a temporary research position; during this time period, he had to develop Coherent Anti-Stokes Raman spectroscopic devices (CARS) for investigating diluted liquid solutions. In 1977, he obtained a position of assistant professor in the frame of a joint collaborative project between the LASIR and the "Laboratoire de catalyse homogène et hétérogène" in Lille, which he joined definitively in 1987. Thanks to the use of the new Raman microprobe "Mole", developed by Prof. Michel Delhaye at the LASIR-Lille (built and commercialized by the Dilor Company in 1975), he became a pioneer in the in situ characterization of oxidic and sulphidic materials used as catalysts for hydrotreating (HDT). As a matter of fact, Raman spectroscopy and hydrotreating catalysis can be considered as the keywords in his academic research activities. A third keyword would be molybdenum, which is likely the most extensively used in heterogeneous catalysis for HDT and oxidative catalytic applications. From 1987 to 1990, Edmond carried out his research at the "Institut français du pétrole" in Rueil-Malmaison, where he developed Electron Energy Loss Near Edge Share Spectroscopy (ELNES) applications on a STEM-VG apparatus. Then, in collaboration with Prof. P.C.H. Mitchell of the University of Reading (UK), Edmond has also been deeply involved in the use of Inelastic Neutron Scattering (INS) and Neutron Compton diffusion (eVS) at the Rutherford Appleton Laboratory for the characterization of heterogeneous catalysts. Further, he did not hesitate to use large synchrotron facilities for conducting in situ studies by EXAFS (X-ray Absorption Fine Structure), XANES (X-ray Absorption Near-Edge Structure) and X-ray anomalous scattering. Edmond Payen had understood that one should characterize a catalyst under working conditions to fully

**Fig. 1.** Edmond Payen at the French Institute of petroleum (1994).

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**Fig. 2.** Edmond Payen today.

understand its behaviour and to be able to improve its properties.

In the second part of his professional career and thanks to the improvements in spectroscopic methods, he introduced and developed new spectroscopic tools, including Raman spectroscopy, consisting in investigating the spectral responses of catalytic materials under working conditions. From the introduction of these new developments, it was possible to get a more precise visualization of the growth of active phases/sites in operando or in situ conditions, which opened up new opportunities to get more insights into reaction mechanisms, despite their complexity and versatility due to the fact that they strongly depend on the composition of the reaction media. Nevertheless, important structural and electronic properties were elucidated regarding mainly modified molybdenum-based catalysts. Particular attention was paid by Edmond Payen to the use of these in situ approaches to understand at the molecular level the genesis of the molybdenum active sites during the different steps of preparation in order to rationalize synthesis protocols. Passionate and convinced, he has been the initiator of a French research project (ANR SAXO), which is at the origin of the Equipex program ROCK, which is a beam line located at the SOLEIL synchrotron machines (located in Saint-Aubin, France) dedicated to the characterization of batteries and catalysts.

During his career, Edmond constantly leaned on new spectroscopic techniques and scientific approaches in addition to molecular modelling tools for depicting nanoscale dynamic processes at the surface of catalytic materials. With more than 200 journal papers, Edmond Payen has received recognition at the national and international level in the field of spectroscopy in catalysis and particularly in hydrotreating catalysis. Although at first glance his research was fundamental, it has a considerable impact on applications and resulted in a lot of contracts with national and foreign chemical industries.

With such a multidisciplinary background, naturally he strongly contributed to the creation, in 2006, of the Unit of Catalysis and Solid State Chemistry (UCCS–UMR 8181) by merging the “Laboratoire de catalyse de Lille” (LCL, UMR 8010) and the “Laboratoire de cristallochimie et physicochimie du solide” (LCPS, UMR 8012). He thus created the biggest chemistry research unit in the north of France, which he has headed for five years and which has reached international renown.

## 1. 1972–1983: The spectroscopist who progressively shifted to catalysis

After the discovery of Raman spectroscopy during his PhD, Edmond Payen had the opportunity to start his research career in connection with new analytical developments by using Coherent Anti-Stokes Raman Diffusion, largely more sensitive than Normal Raman, especially in the case of gas and liquid phases (PhD thesis of B. Clarisse, Lille, 1978). While these original applications did not lead either immediately or in the past three decades to practical developments, it is worth to note that more recent technical breakthroughs gave new opportunities for technological developments, especially in the field of mapping for biological substrates, but also in catalysis [K. F. Domke & al., Angew. Chem. Int. Ed. 51 (2012) 1343–1347]. Through constant efforts and relations with the HORIBA Jobin Yvon Company in order to get new insights into the potentialities of these Raman techniques, Edmond Payen extended their applications in the domain of catalysis. By way of illustration, recent scientific achievements demonstrating the added value of resonance Raman effects and of the ULF technology for characterizing the morphology of the HDS active phases gave him the opportunity to get several invitations to China (2007–2014) for demonstrating the potentialities of Raman spectroscopy in the field of heterogeneous catalysis.

Coming back to the beginning of his professional career, most of the molecular information on the catalysts came at that time from Infrared Spectroscopy. Unfortunately, this technique was inadequate to get relevant structural information at low wavenumber values (below 1000 $cm^{-1}$), the spectral range in which the vibrational modes of the inorganic materials such as heterogeneous catalysts are observed. The introduction of Raman spectroscopy gave him the opportunity to get this molecular information. It is true that obtaining this information, a new description of oxide-supported materials, such as molybdenum supported on alumina currently used as oxidic precursor in hydrodesulphurization (HDS), arose, and the conventional approach of the surface structure currently accepted by the scientific community was totally renewed, emphasizing the fact that these Mo atoms were not dispersed as a monolayer, but more likely as 2D aggregates stabilized as polyoxomolybdate entities dispersed at the surface of the substrate. He showed that hydroxyl groups, contributing to the surface acidic properties, are associated with these oxomolybdate surface species.

The next step in the preparation of the HDT active phases consists of sulphidation of these oxidic precursors, yielding well-dispersed molybdenum disulphide entities that are the active phase in HDT. Once again, Raman spectroscopy provided prominent information related to the formation of nano-sized molybdenum disulphide species. All these research findings were defended for obtaining his doctorate in Physical Sciences in 1983 and represented at that time an original academic viewpoint with possible repercussions in terms of restructuring processes and related economy of oil refining consecutive to the first oil crisis in 1974. Indeed, there was a need to optimize hydrotreating processes to treat crude oils of different origins and compositions.

## 2. 1983–1993: A successful start in the field of catalysis: from fundamental to practical developments

During this period, Edmond Payen intensified his research activities in the field of the synthesis and characterization of hydrotreating catalysts, and especially with the aim to get deeper insight into the molecular description of the solid catalysts at each step of their preparation. At that time, the development of novel catalytic formulation usually resulted from trial and error approaches. Hence, the development of rational methodologies could be considered as a significant breakthrough with possible repercussions on the design of industrial processes dedicated to catalyst production. As a consequence, his academic researches towards a better understanding of the genesis of supported molybdenum and tungsten oxidic and sulphidic phases were achieved in close connection with industrial partners and led to prominent practical issues, since it was demonstrated that significant enhancements of the HDS catalytic properties were possible through the control of the dispersion of molybdenum, even at high Mo loadings. Constant attention was also paid to the sulphidation steps of these oxidic precursors, studying the influence of the activation conditions on the final active phase in the frame of former observations resulting in formation of nano-sized molybdenum disulphide species. Subsequent X-ray photoelectron spectroscopic measurements showed the formation of mixed Co(Ni)MoS active phases, where the promoter (Ni or Co) is localized at the edges of $MoS_2$ crystallites, which led to a detailed model description accounting for anionic vacancies on the edges of $MoS_2$ slabs. This model description has been the starting point of further molecular modelling initiated by Edmond.

In parallel, international collaborations with the Venezuelan Institute of Oil Technology (INTEVEP) gave him the opportunity to investigate the hydrodemetalation of vanadium porphyrins over sulphided cobalt–molybdenum/alumina catalysts. The sensitivity of Raman spectral features to electronic disturbances of adsorbed porphyrin structures once adsorbed led him to propose a mechanism for explaining the poisoning effects during the treatment of these crude petroleum fractions and to evaluate more precisely the consequences in terms of cost efficiency of the existing catalytic processes. Hydrodenitrogenation was also tackled, especially for the treatment of heavy crude oils in order to find out alternative solutions to prevent the current poisoning effects of acid sites. To summarize this period, during which Edmond participated in different national CNRS and European projects (1976–1990), one has to say that significant improvements were gained to optimize the synthesis parameters and develop new synthesis routes. However, important issues remained regarding HDT catalysts related to: (i) the exact nature of the polymolybdate phases, (ii) the improvement of the dispersion of the oxidic and sulfidic Mo (W) entities, and (iii) the optimization of the promotion by Co or Ni and its quantification.

A one-year stay at the French Institute of Petroleum (IFP) for developing new physicochemical characterization techniques under the supervision of Dr. Raymond Szymanski, especially with ELNES microscopic measurements, permitted the characterization of an amorphous nano-sized oxidic structure insensitive to X-ray techniques. Edmond continued to be involved in these developments up to 1990, participating in a collaborative project with the University of Cambridge (Prof. Howie) in which improvements in the detector's sensitivity were conducted. This led to significant improvements in the ELNES spectral resolution.

## 3. 1993–2015: Extension of his panel of expertise and implication in research structuring

A key point in heterogeneous catalysis is clearly the synthesis of novel formulations, more active and stable than the existing ones, and the possibility to evaluate their properties in realistic conditions not so far from the running conditions of industrial plants.

Regarding the first point, and continuing the investigations on the impregnation processes of alumina with molybdenum based solutions, Edmond Payen showed, using various physical techniques, that a partial dissolution of the alumina support occurred during the impregnation, leading to the formation of aluminium six molybdoaluminate (AlMo6) entities that are well dispersed on the surface of the support or precipitated according to the Mo loading and the precursor salt. He showed that the latter phenomenon was at the origin of the limit of good dispersion of molybdenum. Taking into account this phenomenon, he investigated different strategies of preparation of the HDT oxidic precursor in collaboration with industrial companies (Elf, IFP), such as the development of new heteropolycompound precursors (acid or salts) for the preparation of the oxidic precursor, the optimization of impregnation process of shaped support materials, and also the direct synthesis of dispersed nanoparticles of metal oxides. Edmond was also interested in the increase in the promoting effect and thus first developed with the IFPEN a methodology based on XPS analysis permitting to evaluate the true promotion rate of the disulphide crystallites. Then, extensive research studies on pre-activation steps, mainly conducted and patented with the Total Company, led to innovative approaches for increasing the desulfurization of straight run gas oil by modifying the oxidic precursor before its activation with chelating/complexing agents, which improved the dispersion of both the oxide and sulphide phases and the promotion rate by Co or Ni. Interestingly, these findings opened the panel of investigation up to the tuning of new procedures for the regeneration of these new pre-activated HDT

catalysts. With the same company, he also investigated alternative routes for the desulfurization of gas oil such as oxydesulphurization (ODS).

The second point concerned the evaluation of the catalytic performances that make the relevance of academic research at the industrial level. Many academic investigations reported catalytic data on model molecules that could not be capable to restore the representative performances of HDT catalysts in realistic conditions for the desulfurization of diesel at high temperature and high pressure. One of the originality developed in Lille as soon as 1996 has been a validation of the catalytic formulations close to the conditions of industrial processes including shaping. Strong efforts, relevant arguments, and probably the talent of Edmond Payen convinced the political institutions to order the construction of a dedicated building of high technicality for hosting pilot reactors working under conditions close to the industrial ones. This Hall of Catalysis, initiated in 2007, opened in 2011 and still today represents a unique tool in France in the world of catalysis.

In 1997, Edmond Payen became head of the research group "Hydrotreating processes of crude oil", which was transformed later into the group for "Energy production", dealing also with the production of clean diesel fraction by Fischer–Tropsch synthesis. He also initiated the development of new topics dedicated to theoretical calculations and molecular modelling in 1993, which complemented practical achievements, providing theoretical explanations on the geometry and the orientation of disulphide nanocrystals dispersed on alumina and silica. Later on, the influence of the chemical potential of gaseous $H_2$ and $H_2S$ on their stability was investigated within a "groupement de recherché" (GDR) entitled "Dynamique moléculaire quantique appliquée à la catalyse", highlighting the promotional effect of cobalt and leading to a molecular description of the reaction mechanism regarding the removal of sulphur in refractory molecules such as dimethyldibenzothiophene. The European IDECAT network provided him with new opportunities to collaborate on this topic, especially with Prof. R.A. van Santen (University of Eindhoven). These theoretical studies were extended towards hydrodesoxygenation (HDO) reactions, with the aim to develop catalytic systems able to treat simultaneously bio and crude oils in a competitive national project application (French ANR project Ecodhoc, 2007–2011).

Appointed director of the research unit (LCL) in 2001, Edmond contributed to the emergence of a new research group coupling molecular modelling with operando spectroscopy. Conducting a national joint research project (ANR SAXO–2008) in collaboration with the Paris-6 University and SOLEIL synchrotron, Edmond largely contributed to the structuration of this group. His work obtained a strong recognition and he was selected as member of the expert panel at SOLEIL for the project selection and time allocations.

As one of the founders of the new laboratory entitled "Unité de catalyse et chimie du solide", Edmond became the director of this new structure in 2006 till 2010. Despite the time consumed for the management, participating to significant local restructuration at the University, he was also active at the national level as a member of the "Comité national de recherche scientifique" (S 14-CNRS; 2004–2008) and as a member of the "comité scientifique" of the "Institut de chimie" (INC-CNRS; 2008–2011). Edmond thus contributed to the visibility of UCCS, but he was never very far from the laboratory. As Emeritus since 2014, he is still active as an experimenter, working naturally on the implementation of new methodologies in Raman spectroscopy.

## 4. His passion for education at ENSCL

After a position as assistant at the University of Lille – Sciences and Techniques from 1973 to 1984, Edmond Payen was appointed at the "École nationale supérieure de chimie de Lille" (ENSCL) in 1984 and became Professor there in 1992. At the ENSCL, he was in charge of teaching crystallography, general chemistry, and analytical techniques. With the same passion as in research, in the 1990s, he sat up a common centre for physical analysis, gathering thermal analyses, X-ray diffraction, X-ray florescence, NMR, IR spectroscopy, polarography, which was opened to students to carry out research projects. Under his impulsion, classical lab student studies were transformed into research projects. Aware of the need to link catalysis and process and of the need of specialists in the field, in 2004, in collaboration with the "Institut français du pétrole", the "École centrale Lille" and the ENSCL, he developed a masters degree on catalysis and process, which still exists and attracts not only French students, but also people from around the world. Although close to retirement, in the beginning of the 2010s and after benchmarking on the new trends in chemistry, he established at the ENSCL a new specialization on the biomass valorization entitled "Chemistry and sustainable processes for industry", which he headed for two years before becoming Emeritus.

Former students keep the souvenir of a professor with sparkling eyes, a particular humour, always running from one building to the other, but who was a rare teacher who did not consider that all experiments were supposed to work, with whom one could discuss the results freely without the impression to be judged, but just as scientists. For his outstanding achievements at the ENSCL, he was awarded "chevalier des palmes académiques" in 2005.

To sum up, we can say that his students and collaborators have enjoyed working with Edmond likely for his dedication, his scientific rigour and his respect, but also for his ability to set up a friendly atmosphere in which humour is never far from science.

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