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Grammaticakis-Neumann Award Lecture 2014: Protein film photoelectrochemistry of the water oxidation enzyme Photosystem II

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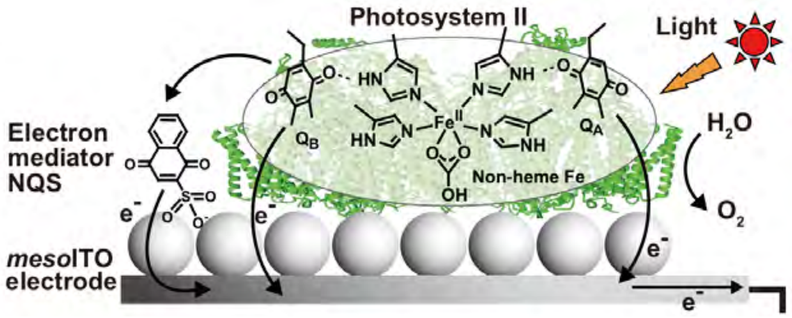
Protein film photoelectrochemistry (PF-PEC) allows for the light-dependent activity of Photosystem II (PSII) adsorbed onto an electrode surface to be studied.[1] We have recently made some progress in the direct integration of PSII into metal oxide electrodes. PSII from *Thermosynechococcus elongatus* was adsorbed on a nanostructured and transparent indium-tin oxide (ITO) electrode for visible light driven water oxidation to O_2 and non-mediated electron transfer was observed at the enzyme-electrode interface (Figure 1).[2] A rational strategy to electrostatically orient and covalently immobilise PSII on the ITO electrode was also developed, resulting in enhanced photocurrent response and film stability.[3] In our initial studies, PF-PEC was shown to provide us with valuable insights into the activity, stability, quantum yields, and interfacial electron transfer pathways of PSII. Recent progress and future prospects of PF-PEC with PSII will be discussed.



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Interplay between complexity and universality in industrial catalysts

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[1]IFP Energies nouvelles

Within the current economic and environmental context, improving the efficiency of catalytic processes is highly mandatory in order to produce cleaner fuels meeting well defined specifications. For that purpose, quantified concepts on the nature of active sites, mechanisms and chemical trends help for the continuous improvement of industrial supported catalysts. The complexity inherent in the multi-component character of such catalysts may challenge the identification of predictive chemical trends (such as volcano curves…) also qualified as “universal trends” [1].

Through relevant examples, this lecture will address the questions of “universality” concepts and complexity of heterogeneous catalysis in an industrial context. For that purpose, combined experimental and theoretical approaches will be presented on various systems: transition metal sulfides (TMS), metals, and aluminosilicates used in refining and petrochemical processes (hydrotreatment, biomass conversion, reforming, hydrocracking...). We first report volcano curves based on quantum descriptors identified for reactions catalysed by TMS and metals [2]. Then, by combining ab initio calculations, advanced characterizations (XAS, IR, STEM-HAADF,…), and model test reactions, we highlight the intricate effects of the support, the size and the morphology of particles in reaction conditions [3,4,5]. These effects still remain at the frontier of the “universality” concept. Hence, this lecture will deliver guides to tackle “universal” and “non-universal” cases by integrating this complexity [6].

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Investigation of factors affecting the crystallisation of zeotype Sn-Beta with elemental mapping

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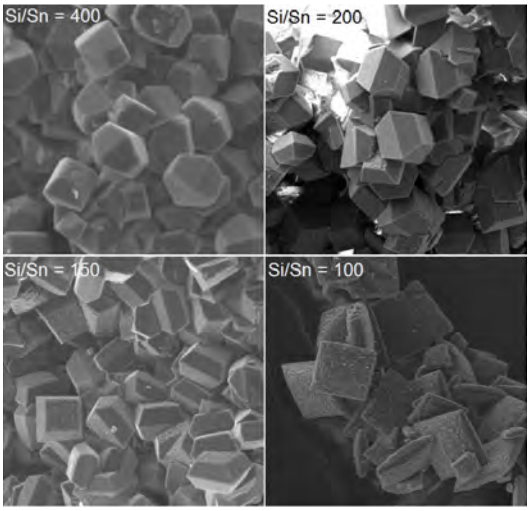
Sn-Beta is a Lewis acidic zeotype material that has been shown to possess interesting catalytic properties for a number of reactions. These include Baeyer-Villiger oxidations, Meerwein-Ponndorf-Verley-Oppenauer redox reactions, isomerisation of monosaccharides and direct conversion of sugars to lactic acid derivatives [1-3]. The catalytic properties are believed to originate from discrete tin atoms incorporated into the microporous framework of the beta zeolite, which possess strongly Lewis acidic properties, in combination with the large accessible surface area due to the microporous channels.

Synthesis of Sn-Beta by direct crystallisation in a fluoride media, is known to produce large Sn-Beta crystals with few imperfections and a hydrophobic interior. The crystallisation time often varies from a few days to many weeks or even months. Typically, the Si:Sn ratio in the resulting Sn-Beta is in the range of 150:1 to 200:1.

Using a combination of elemental mapping and testing of catalytic properties, we have investigated the crystallisation of Sn-Beta in fluoride media by systematically varying the amount of tin in the synthesis gel, the type of tin precurser, as well as the crystallisation time. It was found that the amount of tin in the gel greatly influences the time required for crystallisation and the type of tin precurser is also found to be highly important. Some tin precursers such as nanocrystalline SnO2 are not incorporated into the beta structure at all and the resulting materials do not possess the usual catalytic properties of Sn-Beta. Surprisingly, it was found that the amont of tin also affects the morphology of the resulting Sn-Beta crystals. At zero or low levels of tin, beautiful bipyrimidal crystals were formed, whereas at high tin loading, truncated bipyrimidal crystals forms instead.



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C-H Activation on Tri-Coordinated Cr(III) Silica Surface Sites Initiates Ethylene Polymerization

Murielle F. Delley[1], Francisco Núñez-Zarur[1], Matthew P. Conley[1], Aleix Comas-Vives[1], Georges Siddiqui[1], Olga V. Safonova[2], Christophe Copéret[1] *

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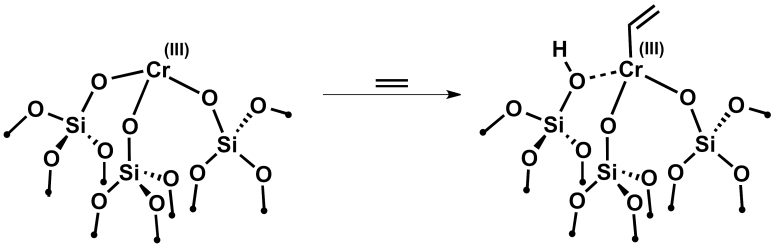
Chromium on silica is the classical Phillips catalyst for ethylene polymerization,[1, 2] used for almost half of the world's polyethylene production. However, the active site and the initiation step is a matter of controversy even after 50 years of research. Recently, we have shown that well-defined dinuclear Cr(III) materials are active ethylene polymerization catalysts, while analoguous Cr(II) materials are not.[3]



Deeper mechanistic insight could be obtained by the preparation of Cr(III) mononuclear sites via a molecular approach using a combination of spectroscopy (IR, EPR, UV/Vis, EXAFS/XANES) and DFT computation. [4] Tri-coordinated Cr(III) sites initiate ethylene polymerization by C-H activation of an ethylene C-H across a Cr-O bond. Propagation of the polymer chain occurs via a Cossee-Arlman mechanism and chain termination via a proton transfer corresponding to the microreverse of the initiation step.

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Transient studies of methane steam reforming over ceria-promoted Rh/Al_2O_3

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Methane steam reforming (MSR) is the principal technology for hydrogen production. A temporal analysis of products (TAP) reactor [1] was used to determine the mechanism of MSR over Rh/Al_2O_3 and $Rh/12CeO_2\text{-}Al_2O_3$ and the role of ceria as part of the support. Transient experiments with alternating water and methane/argon pulses with varied delay between them (5, 73 and 86 s) show differences in the adsorption and reaction characteristics of the catalysts (Figure 1). Water at the catalyst surface reacts with a methane pulse to yield hydrogen and carbon monoxide. The carbon species, formed by reacting methane, react with the following water pulse: addition of water with 5 s delay results in the formation of hydrogen and carbon dioxide over Rh/Al_2O_3. Ceria-containing support enhances partial oxidation of carbonaceous species by water; $Rh/12CeO_2\text{-}Al_2O_3$ shows also formation of carbon monoxide. The addition of water with longer delay after methane pulse does not yield any product over Rh/Al_2O_3 pointing to the stabilization of carbon species at the catalyst surface over time; hydrogen and carbon dioxide are observed over $Rh/12CeO_2\text{-}Al_2O_3$ showing that ceria catalyzes the oxidation of carbon species by water.

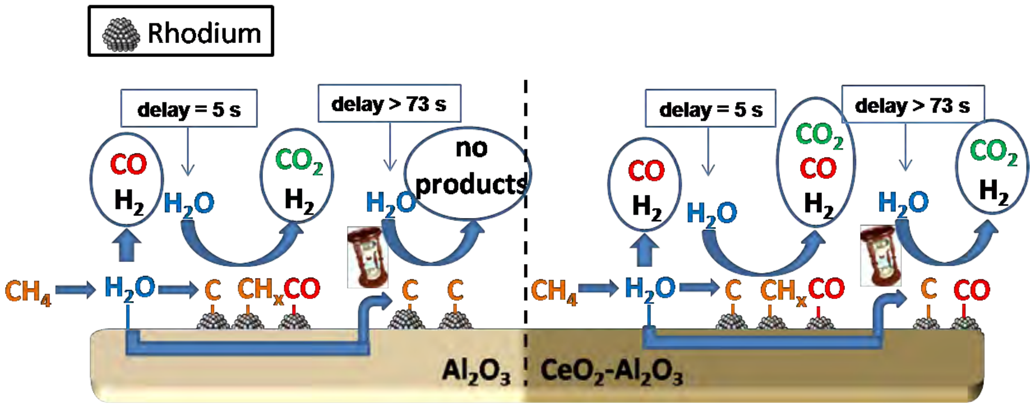

Figure 1: Proposed scheme for the transient experiments with alternating water and methane/argon pulses over Rh/Al_2O_3 and $Rh/12CeO_2\text{-}Al_2O_3$.

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Mesopore quality determines the lifetime of hierarchically-structured zeolite catalysts

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Deactivation resulting from micropore blockage due to coking majorly limits the lifetime of zeolite catalysts in the production of chemicals and fuels. Significantly improved performance can be achieved through hierarchical structuring of the zeolite porosity,[1] yet remarkably no relation has been established between the mesopore architecture and the catalyst lifetime. Here, overcoming synthetic and analytical obstacles, we introduce a top-down demetallation approach to locate mesopores in different regions of MFI-type crystals with identical bulk porous and acidic properties. In contrast, other well-established bottom-up strategies such as carbon templating and seed silanization fail to yield materials with matching characteristics. Advanced characterization tools capable of accurately discriminating the mesopore size, distribution, and connectivity are applied to corroborate the concept of mesopore quality. In particular, positron annihilation lifetime spectroscopy proves powerful to quantify the global connectivity of the intracrystalline pore network which, as demonstrated in the conversions of methanol or of propanal to hydrocarbons, is strongly linked to the lifetime of zeolite catalysts (Fig. 1). The findings emphasize the need to aptly tailor both the mesopore and active site quality of hierarchical materials for maximal catalytic advantage.

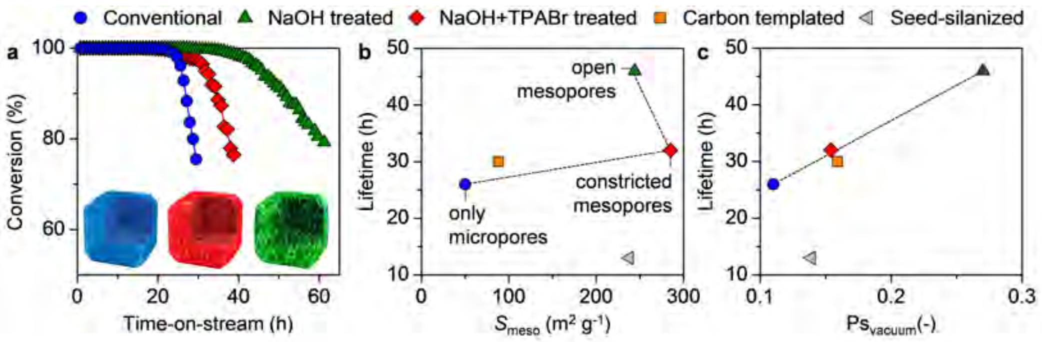

Figure 1. Methanol-to-hydrocarbons performance of hierarchical zeolites (a) in relation to their external surface area (b) and pore network connectivity (c).

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1D and 2D Tuning of Cobalt-based Water Oxidation Catalysts

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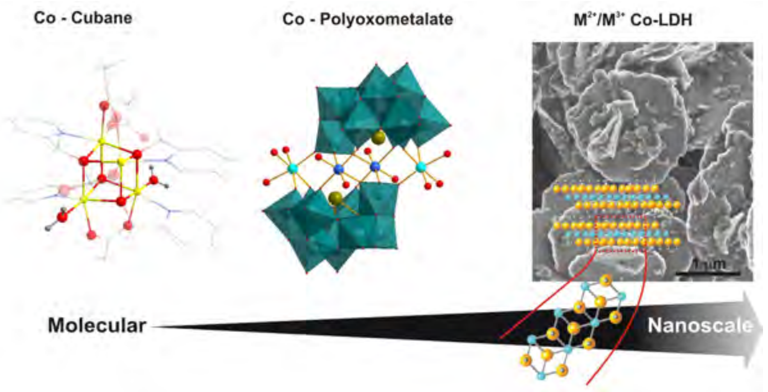
[1]University of Zurich

Efficient Co-based water oxidation catalysts (WOCs) inspired by the cuboidal {$CaMn_4O_5$} oxygen evolving complex (OEC) of photosystem II (PSII) are in the focus of current artificial photosynthesis research [1]. Investigation of their oxygen evolution mechanisms and true active species poses new challenges [2].



We will herein present a comprehensive approach towards structure-activity relationships of Co-WOCs through parallel development of novel Co-cubanes as PSII mimics, nanoscale Co-polyoxometalates (POMs) and Co-containing layered double hydroxides (LDHs).

First, we studied the influence of molecular core-shell combinations on the WOC activity of Co-POM-WOCs [3]. The novel tungstobismutate water oxidation catalyst $[\{Co(H_2O)_3\}_2\{CoBi_2W_{19}O_{66}(OH)_4\}]^{10-}$ outlines the crucial influence of subtle core disorder on the WOC activity among a series of isostructural Co/Mn-containing POMs. POM-WOCs furthermore form complexes with positively charged photosensitizers which are challenging to investigate. Aiming for neutral molecular WOCs, we newly embedded a $\{Co(II)_4O_4\}$-cubane core into a ligand architecture of unprecedented flexibility as a key step towards PSII-OEC [4]. Bio-mimetic advantages of the novel Co-WOC $[Co^{II}_4(hmp)_4(\mu\text{-}OAc)_2(\mu_2\text{-}OAc)_2(H_2O)_2]$ include: (1) presence of high-spin Co(II) centers in close analogy to the Mn centers of PSII, (2) enhanced catalytic performance through ligand exchange and deprotonation, and (3) first experimental input for modeling new water oxidation pathways.

Expansion of the active cuboidal $[M^{z+}{}_{1-x}M^{3+}{}_x(OH)_2]^{q+}$ ($M^{z+} = Co^{2+}$) moiety into 2D layered systems is demonstrated for new photo- and electrocatalytic Co-based LDH-WOCs.

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Structured Fe_2O_3 –based Catalyst for Reduction of Nitroarenes under Mild Conditions

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[1]EPFL Lausanne

Functionalized anilines are widely used as intermediates for the production of agrochemicals, pharmaceuticals, dyes and pigments. Traditional processes, e.g. Béchamp's reaction or reduction by sulphides, have gradually been replaced by selective and environmentally friendly catalytic hydrogenations. The benchmark catalysts are mostly based on supported noble metals (Pt, Ir, Ru, etc.) and are carried out at high hydrogen pressures up to 50 bars [1]. Catalytic hydrogen transfer hydrogenation using different liquid reducing agents as hydrogen source and non-precious metals as catalysts allows to work at low temperature and atmospheric pressure being a valuable alternative [2, 3].

Herein, we report a development of structured catalyst based on Fe_2O_3 nanoparticles (NPs) supported on activated carbon fibres (ACF) for selective transfer hydrogenation of substituted nitroarenes (NAr) into corresponding anilines under mild conditions using hydrazine as a reducing agent (**Fig. 1**). ACF materials have high specific surface area and open homogeneous 3D macrostructure. They are easy to handle, to separate from the reaction mixture after a reaction and due to low resistance to fluid flow are suitable for continuously operated reactors [4].

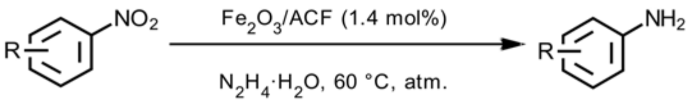

Fig. 1. Reduction of nitroarenes to corresponding anilines

Catalyst characterization (BET, SEM, TEM and XRD) revealed monodispersed Fe_2O_3 NPs (*d* 2 nm) within the ACF micropores. Catalyst activity and selectivity were studied as function of the reactions conditions (temperature, NAr concentrations, etc.). For a wide range of functionnalized NAr full conversion with high selectivity (S98%) towards corresponding anilines was achieved within 1-2 hours under optimal conditions.

Acknowledgments: The authors gratefully acknowledge the financial support provided by the Swiss National Science Foundation (grant agreement no.: 200020_149869)

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NH_3 promoted formic acid decomposition over monolithic Au/TiO_2 catalyst: Rate enhancement without NH_3 oxidation

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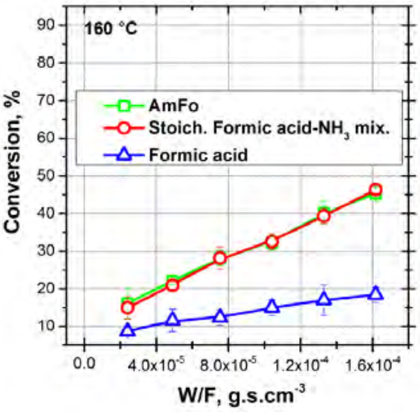
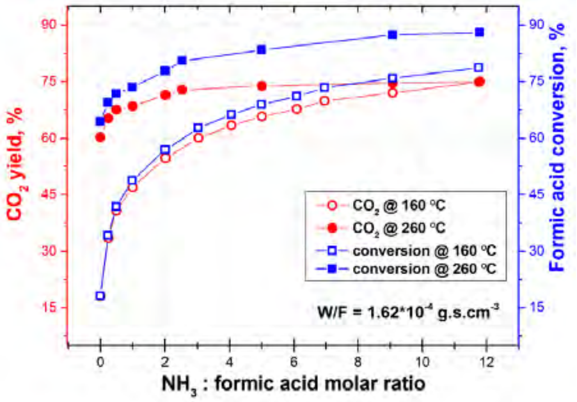
Despite the wide-spread implementation of the selective catalytic reduction (SCR) process with urea in automobiles, there is much interest in replacing this compound with alternative NH_3 precursors, such as concentrated guanidinium formate, ammonium formate (AmFo) and methanamide solutions, which are more thermally stable, freeze at lower temperatures, have higher NH_3 storage capacities, and decompose more selectively.[1.2] AmFo is experimentally the simplest choice to study the activity and behaviour of catalysts for the decomposition of the aforementioned precursors under actual conditions.[3] Recently, we demonstrated Au/TiO_2 as a highly active and uniquely selective catalyst for AmFo decomposition without NH_3 oxidation.[4] Since, AmFo thermolyzes into NH_3 and formic acid in the gas phase, it is important to understand the effect of NH_3 on formic acid decomposition. In this context we have performed formic acid and AmFo decomposition under realistic exhaust gas conditions over 0.5 wt% Au/TiO_2 anatase monolithic catalysts using different GHSVs in the range of 57,000 h^{-1} to 350,000 h^{-1} ($2.4*10^{-5}$ g•s•cm^{-3} ≤ W/F ≤ $1.62*10^{-5}$ g•s•cm^{-3}) and temperatures between 160 ºC and 300 ºC. A systematic investigation of NH_3 influence on formic acid decomposition revealed a beneficial influence of NH_3 on the reaction rate and the CO_2 yield for temperatures below 300 ºC (Fig. 1& 2). No NH_3 oxidation occurred at any of the studied temperatures and space velocities. With the introduction of NH_3 at a concentration of only 0.25 molar equivalents, the pseudo-first-order rate constants for formic acid decomposition experienced close to 110% and 15% increase at 160 ºC and 260 ºC, respectively (GHSV = 57,000 h^{-1}, W/F = $1.62*10^{-4}$ g•s•cm^{-3}). Using the same contact time, increasing the NH_3 to formic acid molar ratio from 0 to 12 led to a steep increase in the CO_2 yield from 18% to 75% at 160 ºC, while a relatively smaller rise from 60% to 75% was observed at 260 ºC. Activity testing of bare TiO_2 revealed that the presence of gold is critical for realization of this positive NH_3 effect.





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Lactic acid production from biomass: a new chemocatalytic process compared to fermentation by LCA analysis

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In recent years, the widening application of the bio-based polylactide plastic has determined an increasing demand for lactic acid (LA). The current production of the latter relies on the batch fermentation of sugars, which suffers from limited productivity and scalability (Fig. 1, left). New chemocatalytic routes are emerging in order to supply the growing market. The Lewis-acid catalyzed isomerization of dihydroxyacetone (DHA), an oxidation product of glycerol, has attracted particular interest. If the reaction is performed in water LA is attained directly, while if alcohols are used as the solvent a second step is required in order to hydrolyze the alkyl lactates (AL) obtained (Fig. 1, right).[1] In spite of some promising lab-scale results, the industrial viability of these alternative routes has never been assessed. Herein, we (*i*) introduce a novel and highly performing catalyst, *i.e.* Sn-MFI, for the batch production of LA and AL from concentrated DHA solutions, (*ii*) explore the possibility to conduct the reactions under the industrially more attractive flow operation, and (*iii*) compare the chemocatalytic processes to the enzymatic route with respect to cost and environmental footprint by life cycle analysis.

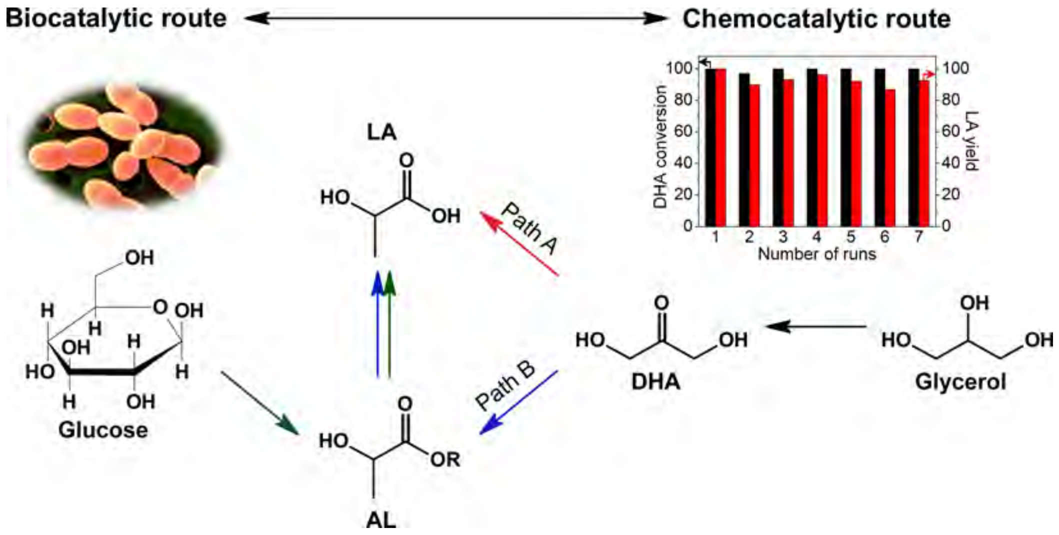

Figure 1. New chemocatalytic route (left side) *versus* the current industrial biocatalytic process (right side) for the production of lactic acid.

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