



Title	Advanced approaches for the synthesis and the exploitation of hydrogen peroxide
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Proponent	Paolo Centomo
Research Group	Polymeric Materials for Advanced Catalysis
Contact	web:
	email: paolo.centomo@unipd.it
Co-Proponent	Andrea Biffis
Research Group	Applied Organometallic Chemistry
Contact	web: www.organometallics.it
	email: andrea.biffis@unipd.it

International Secondment	
PI	Tapio Salmi
Institute	Abo Akademi Finland
Place, country	Turku, Finland
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Project description (2 page max):

The oxidizing agents currently employed in chemical manufacturing are generally noxious to living organisms and to the environment. Accordingly, for more than three decades there has been a surge of interest in the production and application of hydrogen peroxide as a “green” oxidant [1], forming only water as reduction byproduct. However, the commercial use of H_2O_2 in chemical manufacturing is still relatively limited, mainly due to its relatively high cost. In fact, its production currently relies almost exclusively on the autooxidation (AO) of an alkylanthraquinol obtained from the hydrogenation of the parent quinone, that is a highly optimized process, but appears affordable only for a large scale production. Major contributions to its relatively high costs come from the production of the alkylanthraquinone (recycled but required in large amount), the use of an environmentally unfriendly solvent mixture and the downstream extraction and concentration (up to 70%) of HP. This energy intensive operation is required for the efficient dispatch of the product from the production sites, even though diluted solution of H_2O_2 are needed for the final uses. In this regard, the synthesis of H_2O_2 from its elements (direct synthesis) is considered as the most convenient alternative to the AO process for the development of delocalized, small-to-medium scale H_2O_2 plants [1]. However, the handling of H_2/O_2 mixtures would be a major safety issue; moreover, wide-spread diffusion of small scale direct synthesis plants would require an extended network for H_2 transportation, another safety issue, or local facilities for its production.

The problem of selectivity is of paramount importance in the direct synthesis, as water is not only the thermodynamically favoured product, but also can be produced by dismutation and hydrogenation of H_2O_2 . The most commonly employed system for promoting the direct synthesis of HP are Pd-based mono- or bi-metallic catalysts, usually highly dispersed on porous substrates. The process is carried out in the presence of a protic solvent, typically methanol, that is cheap and provides a good solubility of the gaseous reagents and of a variety of organic substrates. This not only ensures a good catalytic performance, but also makes possible the direct exploitation in technological applications of the produced HP solutions. From a plant engineering point of view, several solutions have been proposed, including batch and continuous flow reactors. In the frame of this project, semi-batch reactors operating at ambient and moderate pressure (up to 10 bar) are employed: under these conditions, the gaseous reagents are continuously fed into the reactor containing the reaction mixture (Figure 1) [2]. The large volume of the reaction mixture, allowing the collection of several samples for the measurement of the amount of produced H_2O_2 [3], and the inline analysis of the outgoing gaseous phase (with a μ -gaschromatograph) make possible to define in detail the reaction profile.

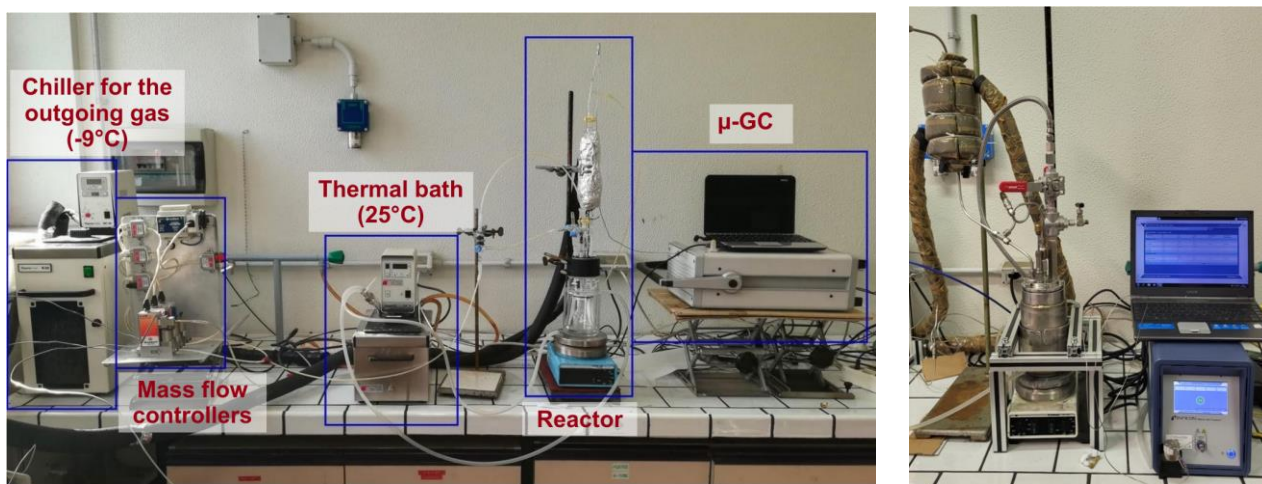


Figure 1. Ambient (left) and moderate pressure (right) reactors for the direct synthesis of H_2O_2 .

Over the years, our research group gained an appreciable experience in the use of cross-linked organic polymers [4] (hereafter referred to as resins) as supports for heterogeneous metal catalysts. Resins are much

less popular catalytic supports in comparison with inorganic materials, in view of their lower thermal and mechanical stability. However, under mild reaction conditions, as in the case of the direct synthesis of H_2O_2 , resins can easily withstand them and be successfully employed. Resins are available in very different chemical structures and textures and can be conveniently tailor-made by a “molecular engineering” approach [4]. Moreover, catalytic reactions usually occur in their interior and the micro-environment of the polymer framework can positively affect the outcome: as the result, resin supported Pd catalysts are among the most promising systems for the direct synthesis of HP [1,2]. Recently, we proposed the exploitation as the catalytic support for Pd nanoparticles of a novel mesoporous form of polydivinylbenzene, ensuring a remarkable catalytic performance thanks to its high accessibility: this makes possible an efficient back-diffusion of the produced H_2O_2 towards the bulk solution, limiting its hydrogenation to water [2].

In this project, we propose to study in detail the reactivity of mesoporous styrenic supports and to couple the direct synthesis reaction with technologically relevant oxidation reactions. In fact, styrenic cross-linked polymers show a significant radical reactivity under reaction conditions, suggesting a possible role in the activation of molecular oxygen used as the reagent [5]. This reactivity, observed in a preliminary investigation not only for catalysts supported on mesoporous polystyrene but also for those supported on commercial polystyrene-divinylbenzene resins, is poorly investigated for the direct synthesis and opens new perspectives in the production of H_2O_2 . In fact, the radical activation of molecular oxygen on the catalytic support could be in principle exploited for increasing the performance of Pd catalysts in the formation of H_2O_2 , in a process that involves, beside the direct reaction between H_2 and O_2 , also the hydrogenation of hydroperoxide intermediates formed on the surface of the polymer framework [4]. A similar approach can be reasonably applied also to Pd catalysts supported on activated carbon, the most popular catalytic system for the direct synthesis, to improve its performance. To enhance the radical activity of the catalysts, the direct synthesis of H_2O_2 can be performed also under UV irradiation condition. Finally, the effect of selectivity enhancers on these catalytic systems will be investigated, with particular attention to novel cheap and non-corrosive promoters, such as acetonitrile and dimethylsulfoxide, recently proposed by our research group [6].

In this PhD project, the direct synthesis of H_2O_2 will be also coupled with a technologically relevant oxidation reaction in a one pot process. On the one hand, this approach is expected to be efficient, as the produced H_2O_2 can be immediately used, before it can be hydrogenated to water. On the other hand, the reaction conditions of both direct synthesis and the subsequent oxidation of the organic substrate have to be carefully tuned, in order to maximize the oxidation performance. To this end, particularly attractive appears the hydroxylation of aromatic compounds with H_2O_2 , typically promoted by titanium silicalite [7]. Novel catalytic systems for the one pot hydroxylation of aromatics with H_2 and O_2 can be obtained either by preparing suitable physical mixtures of resin based Pd catalysts for the direct synthesis and titanium silicalite, or by generating Pd nanoparticles inside titanium silicalite, to obtain bifunctional catalysts.

References

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