105a Progresses in Membrane Reactors (Invited Keynote Speaker)

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Catalytic reactions are already intensively used in chemical industry, energy conversion, wastewater treatment and in may other cases. However the necessity to realize the process intensification strategy calls for additional and substantial developments also in this field. In this perspective, the application of membrane technology in catalysis offers interesting opportunities, from both an environmental and an industrial point of view [1]. The combination of advanced molecular separation and chemical conversion, realized in a catalytic membrane reactor (CMR) permits the catalyst recycling; moreover the selective transport properties of the membranes can be used to shift the equilibrium conversion (e.g. esterification reaction), to remove selectively products and by-products from the reaction mixture, to supply selectively the reagents (e.g. oxygen for partial oxidation reactions). A special category of membrane reactors exists when the membrane defines the reaction volume, e.g. by providing a contacting zone for two immiscible phases (phase transfer catalysis) excluding solvents and thus rending the process environmentally more attractive. The first applications of catalytic membrane reactors concerned high temperature reactions carried out with inorganic membranes. These membranes, characterized by higher chemical and thermal stability with respect to polymeric membranes, still today suffer from some important drawbacks: high cost, limited lifetime, difficulties in reactor manufacturing (delamination of the membrane top-layer from the support due to the different thermal expansion coefficients) . On the other hand, the use of polymeric membranes in catalytic membrane reactors is increasing in interest [2]. The cost of polymeric membranes is generally low, and the preparation protocols allow a better reproducibility; moreover, the relatively low operating temperatures are associated with a less stringent demand for materials used in the reactor construction. In general, polymeric membranes are less resistant to high temperatures and aggressive chemicals than inorganic. However, polymeric materials resistant under rather harsh conditions – e.g. polydimethylsiloxane, Nafion, Hyflon, polyvinylydene fluoride - are today available. Moreover, many reactions of relevant interest in fine chemical synthesis or in water treatment take place under mild conditions.

The application of catalytic membrane reactors appears of particular interest in several areas such as: oxidation reactions and enantiomeric productions. Novel heterogeneous photooxidation catalysts, performing in water with O2, have been prepared by embedding polyoxotungstates in polymeric membranes. These polymeric catalytic membranes have been successfully applied in the photooxidation of organic substrates in water providing stable and recyclable photocatalytic systems with different and tuneable properties depending on the nature of the polymeric environment [3]. The use of plasma techniques for the heterogenization of these catalysts on membrane surface, is also under investigation in order to increase the ratio substrate conversion/amount of catalyst. The incorporation of homogenous Ti(IV)/trialkanolamine catalyst in polymeric membranes has been also investigated as heterogeneous catalysts for the stereoselective sulfoxidation of alkyl-aryl sulfide and the oxidation of secondary amines to nitrones by alkyl hydroperoxides [4].

Biocatalytic membrane reactors can also be used in production, processing and treatment operations. The trend towards environmentally friendly technologies makes these units particularly attractive because of their ability to operate at moderate temperature and pressure, and to reduce the formation of by-products. Enzymes, compared to inorganic catalysts, generally permit greater stereospecificity, and higher reaction rates under milder reaction conditions. Relevant applications of biocatalytic membranes reactors include: production of new or better foodstuffs, in which desired nutrients are not lost during thermal treatment; novel pharmaceutical products with well-defined enantiomeric compositions; wastewater treatment. Methodologies for the preparation of emulsions (sub-micron) oil in water have been developed and such emulsions have been used for kinetic resolutions in heterogeneous systems catalyzed by enantioselective enzyme. A catalytic reactor containing membrane immobilized lipase has been realised for optical resolution of racemic naproxen in biphasic enzyme membrane reactors. In this reactor the substrate has been fed as emulsion. The distribution of the water organic interface at the level of the immobilized enzyme has remarkably improved the property of transport, kinetic and selectivity of the immobilized biocatalyst [5].

An innovative potential application of membrane technology in catalysis and in catalytic membrane reactors, is the possibility to produce catalysts crystals with a well defined size, size distribution and shape, by membrane crystallization technique [6], eventually in a continuous mode.

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