Catalytic membrane and catalytic membrane reactors: an integrated approach to catalytic process with an high efficiency and a low environmental impact

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Membrane engineering has been doing huge progresses in the last few decades promoting some membrane operations to dominant technologies. Seawater and brackish water desalination, proton conducting membranes in fuel cells systems, membrane based artificial organs, non cryogenic nitrogen separation, are few well recognized examples.

Process engineers have now the possibility to integrate, not only molecular membrane separations in their production lines, but also membrane contactors and catalytic membrane reactors (CMRs).

New catalyst design based on the heterogenization of catalysts and bio-catalysts in membrane systems, is becoming an attracting possibility.

Advantages are not only the integration of molecular separations of products and reactants with chemical conversions, but also an easier recovery of the catalyst, possible controlled supply of the reactants and controlled removal of the products, new reaction mechanism, etc.

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 polluting solvents and thus making the process environmentally more attractive.

Interesting applications of the CMRs have concerned high temperature reactions using inorganic membranes characterized by an high chemical and thermal stability. Examples include zeolite, mixed ion- and electron-conducting solid oxides membranes, Pd and silica membrane.

The use of polymeric membranes in CMRs is also of increasing interest. The cost of the polymeric membranes is generally lower in comparison with inorganic ones and the preparation protocols allow a better reproducibility.

In general, polymeric membranes are less resistant to high temperatures and aggressive chemicals than inorganic membranes, however polymeric materials resistant under rather harsh conditions – e.g. polydimethylsiloxane, Nafion, Hyflon, polyvinylidene fluoride (PVDF) - are today available. Moreover, many reactions of relevant interest in fine chemical synthesis or in water treatment take place under mild conditions.

Interesting results have been already reached in the production of specific enantiomers with quite high enantiomeric excess using bio-catalytic membrane reactors. A multiphase enzyme membrane reactor has been developed by immobilizing the lipase from Candida rugosa in a polymeric membrane in presence of a stable and uniform oil-in-water emulsion prepared by membrane emulsification. The kinetic resolution of the naproxen esters was investigated showing that the presence of emulsion within the membrane improved the catalytic activity and the
enantioselectivity of the immobilized enzyme as well as the transport rate of the hydrophobic reagent through the hydrophilic membrane [1].

Novel catalytic membranes have been designed and developed by the heterogenization of the photocatalyst decatungstate (W_{10}O_{32}^{4-}) in polymeric fluorinated membranes made of PVDF or Hyflon.

These hybrid membranes have been successfully applied in the aerobic photo-oxidation of organic pollutants in water [2] and in partial oxidation reactions [3], providing stable and recyclable photocatalytic systems.

The photocatalytic composite membranes are characterized by different and tuneable properties depending on the nature of the polymeric micro-environment in which the catalyst is confined.

Particular relevance has been given to the chemical-physical characterization of the catalytic membranes because the understanding of the properties and behavior of these functionalized materials on nanometric scale is fundamental in order to exploit their use as heterogeneous catalysts.

It has been evident the influence that membrane morphology, membrane chemical properties, membrane interface phenomena, can have on the overall catalyst behaviour in these systems.

Catalyst stability and activity has been positively influenced by the polymeric micro-environment in which it is confined; moreover the selective separation function of the membrane results in enhanced performance in comparison with homogeneous reactions.

Interesting results have been also obtaining using inorganic catalytic membrane in high temperature reactions. For example water gas shift reaction (CO + H_2O = CO_2 + H_2) for hydrogen production was studied in a catalytic membrane reactor using a supported silica membrane. A CO conversion higher than the thermodynamic equilibrium of a traditional reactor was obtained thank to the selective hydrogen permeation through the membrane [4].

The possibility of an interesting new catalyst design, based on the formation of mono-dispersed catalytic nano-crystals obtained by membrane crystallizer [5], represent one more example of innovative contribution of membrane science in this field.

References: