

Review Article- Nanoreactors

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Abstract- Sustainable and environmentally benign production are key drivers for developments in the chemical industrial sector, as protecting our planet has become a significant element that should be considered for every industrial breakthrough or technological advancement. As a result, the concept of green chemistry has been recently defined to guide chemists towards minimizing any harmful outcome of chemical processes in either industry or research. Towards greener reactions, scientists have developed various approaches in order to decrease environmental risks while attaining chemical sustainability and elegance. Utilizing catalytic nanoreactors for greener reactions, for facilitating multistep synthetic pathways in one-pot procedures, is imperative with far-reaching implications in the field. This review is focused on the applications of some of the most used nanoreactors in catalysis, namely: (polymer) vesicles, micelles, dendrimers and nanogels. The ability and efficiency of catalytic nanoreactors to carry out organic reactions in water, to perform cascade reaction and their ability to be recycled will be discussed.

Keywords- green chemistry, nanogels, micelles, polymersomes, covalent system,

I. INTRODUCTION

It is widely acknowledged that “the best solvent is no solvent”; however, running a reaction under neat conditions is very challenging from the points of view of mass transfer and temperature gradients. Therefore, sustainable chemical technologies are often related to the use of a green non-harmful solvent, water. In principle, green chemistry refers to the employment of raw material (substrates) in an efficient manner, decreasing the resulting waste or undesired byproducts, and using cheap and environment friendly solvents (i.e., water). Generally, using water as a solvent is an acceptable choice for green chemistry. Indeed, water is attractive from both economic and environmental points of view, and is not taken into account when the E-factor (defined as mass ratio of waste to desired product) for a chemical process is determined. This is to be true for chemical processes where the utility of water is limited to the work-up at the end of the process and not when used as a reaction

medium. However, it should be noted that the utility of water as a reaction medium is the safest, but not the greenest choice. Unfortunately, most organic compounds and catalysts are not soluble in water, limiting its utility for most reactions. For this reason, scientists across academia and industry have proposed many solutions in order to maximize the outcome of reactions (i.e., yields, enantioselectivities, etc.) in water and, thereby, harness its utility for further applications. The abovementioned issues are particularly relevant in the field of asymmetric catalysis, which besides overcoming catalyst compatibility also has to deal with cost issues.

OBSERVATION

1. Homogeneous vs heterogeneous catalysis

Catalysis, in general, is divided into two major types, homogeneous and heterogeneous. In homogeneous catalysis catalyst and substrates are both present and molecularly dissolved in the same phase (typically a liquid phase). Homogeneous catalysis involves the use of biocatalysts (enzymes), organocatalysts and metal catalysts. Catalysis is defined as heterogeneous when catalysts are in an aggregated state, and are thus in a different phase than the reactants. Heterogeneous catalysts typically consist of a solid carrier, the so called “support”, on which catalytic sites are dispersed. Homogeneous catalysis is generally performed under milder operative conditions than heterogeneous catalysis. In fact, heterogeneous catalysts generally possess very high decomposition temperatures (above 100 °C). The presence of a solid phase often results in the formation of temperature gradients when using high temperatures, which leads to an increase in reactant diffusion and a consequent hampering of mass transfer.

2. Self-Assembled Nanoreactors

Self-assembled nanoreactors are macromolecular architectures that are non-covalently assembled from their constituent building units. Such nanoreactors allow for physical confinement of catalysts, shielding them from their surroundings. Compartmentalization of catalysts in supramolecular nanoreactors is advantageous from kinetic

(faster catalytic process) and thermodynamic (lower transition state of reaction) catalysis points of view. Segregation and isolation of catalysts insidenanoreactors guarantee, in most cases, a valuable platform for catalyst recycling . In the following section we will discuss the utility of some of the well-established catalytic nanoreactors towards green(er) chemistry .

2.1. Micelles

Micelles are supramolecular architectures that are assembled of amphiphilic molecules . Above the critical micellar concentration (CMC), surfactants with the appropriately designed hydrophilic head(neutral, anionic and cationic) and hydrophobic chain organize themselves in micelles . Micelleshave been extensively studied and their utility ananoreactors is well-established . Varioumicellar morphologies can be obtained depending on the ‘packing parameter’ , which is defined as $p = v/a_0 l_c$, where v is the volume, l_c is the length of the hydrophobic chain and a_0 is the optimal areaof the head groups . As a general rule, if $p \leq 1/3$ spherical micelles are obtained, while cylindricalmicelles, or the so-called worm-like micelles, form when $1/3 \leq p \leq 1/2$.

Catalysis in micelles:

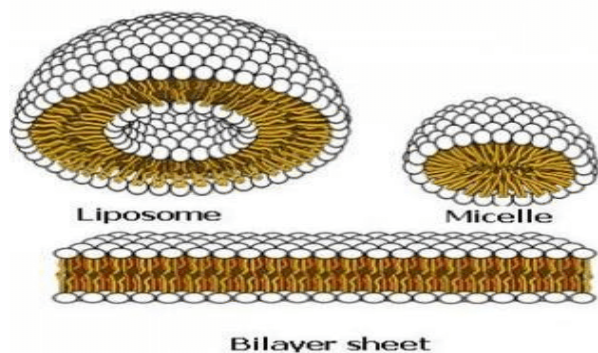


Fig no 1: Catalysis micelles

Micelles as nanoreactors have been extensively used in organic synthesis , allowing reactions in water with better yields and easier catalyst recover than traditional processes. Lipshutz and co-workers have successfully exploited micelles not only asnanoreactors, but as an outstanding platform for achieving greener organic reaction. They have shown, for example, C–N cross-coupling reactions between heteroaryl bromides, chlorides or iodides and carbamate, sulfonamide or urea derivatives to be successfully realized in water using palladium-loaded TPGS-750-M (dl- α -tocopherol methoxypolyethylene glycol succinate) micelles Moreover, this micellar catalytic system allowed for catalyst recycling,

minimizing he amount of the used organic solvent and generated waste .

2.2. Polymeric vesicles

Polymeric vesicles or polymersomes are synthetic bilayered hollow architectures that are self-assembled from amphiphilic block copolymers . The synthetic nature of polymersomes allows for facile tuning of their properties such as size , membrane permeability and stability . Various copolymers have been reported fo polymersome formation such as poly(ethylene glycol)-b-polystyrene (PEG-b-PS) , polystyrene- polyisocyanopeptide (PS-b-PIAT)and poly(N-isopropylacrylamide)-b-poly(ethylene oxide) (PNIPAM-b-PEO) . The term “polymersomes” is derived from liposomes because of the structural resemblance. Compared to liposomes, polymersomes aremechanically robust vesicles and therefore considered to be highly attractive for nanoreactor applications . Polymersomes comprise an aqueous lumen and hydrophobic membrane. Such hydrophilic and hydrophobic compartments are capable of accommodating hydrophilic (e.g., enzymes) or hydrophobic catalysts (e.g., metal catalysts) in their lumen or bilayer, respectively.

Catalysis in polymersomes:

Polymersomes have been most often used as biocatalytic nanoreactors . Polymersome nanoreactors were also employed in Pickering emulsions [83]. Pickering emulsions are emulsions stabilized by colloidal particles that adsorb at the water–oil interface. They are more stable than classical emulsions and do not require the usage of small molecule surfactants. This is a big advantage in downstream processing and product and catalyst recovery. The enzyme *Candida antarctica* lipase B (CalB) was encapsulated in the lumen of the polymersomes or in the Pickering emulsion water droplet.

3. Covalent Systems

3.1. Dendrimers

Dendrimers are a class of highly branched molecules with high degree of symmetry . They consist of different generations in which every generation is twice the molecular weight of the previous one. Dendritic architectures comprise three regions: a core, inner shell and outer shell . The properties of dendrimers such as hydrophobicity can be tuned by varying their initial molecular components or the number of generations they possess . They can assemble in a spherical shape, and within the three-dimensional structure, an interior void is present wherein to accommodate other molecules .

Catalysis in dendrimers:

The controlled synthesis of dendrimers and their applications as nanoreactors and catalyst carriers have been extensively studied over the last decades. Fan and co-workers incorporated a bis(oxazoline)-copper(II) complex in the hydrophobic core of a polyether dendrimer. The copper catalytic complex was used to carry out asymmetric Mukaiyama aldol reactions. Although this system did not result in any substantial improvements in yields or enantioselectivities, it allowed for facile catalyst recovery and recycling. Dendrimers were also used to encapsulate bimetallic catalysts to attain highly selective reactions.

3.2. Nanogels

Nanogels are hydrophilic polymer networks which can swell in the presence of water. They can be crosslinked by either chemical bonds or physical methods, such as non-covalent interactions, entanglements and crystalline domains. The nanogels display excellent swelling behavior and are shape resistant. Due to these unique properties they have mostly been studied as materials in biomedical applications such as controlled drug delivery. Nanogels show promise as nanoreactors as they not only are colloidal stable particles in water but also can be prepared from a wide range of components and in many different sizes and shapes. They have been used for the templated synthesis of metal nanoparticles, via which the shape and size of the nanogel directed the formation of the corresponding particle with similar morphology.

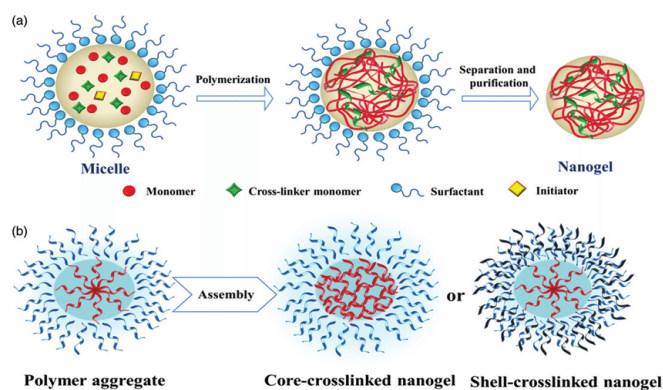


Fig no 2: Nanogel

Catalysis in nanogels:

Nanogels have intrinsic properties that make them well suited for green chemistry. Water-compatible gels are usually based on poly(N-isopropylacrylamide) (PNIPAM), poly(N-vinylcaprolactam) (PVCL) or other water-soluble

polymers. For instance, PNIPAM is a thermo-responsive polymer, which has a lower critical solution temperature (LCST) of 32 °C. Above the LCST, individual polymer chains switch from a swollen coil configuration to a collapsed globular one, providing a nano-environment that is suitable for either hydrophobic or hydrophilic substrates. Water forces PNIPAM brushes to become hydrophobic, acting as a suitable environment for most organic reactions; it allows hydrophobic substrates to diffuse towards the encapsulated catalysts, leading to a concentration effect that directly contributes to an efficient aqueous reaction. The preparation of catalytic nanocomposite hydrogels has been widely reviewed. Several examples showing their utility as nanoreactors for various reactions such as coupling, oxidation and reduction reactions have been reported.

III. CONCLUSION

In this review we have discussed the utility of supramolecular polymersomes, micelles, dendrimers and nanogels in catalysis. Over the past decades, many groups have demonstrated the specific features which make these nanoreactors an advantageous choice for chemical synthesis. In particular, they combine a high active surface area with a good dispersion in solution and therefore are ideal structures for facile diffusion of reactants. Furthermore, the compartments protect the catalyst from undesired interactions with the environment, which can be either the solvent, specifically water, or other catalytic species. As a result they allow reactions to proceed in water and often at room temperature, with excellent yields and selectivities, which traditionally can only be achieved by performing catalysed reactions in organic media.

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