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Multivalent dendritic catalysts in organometallic catalysis

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ABSTRACT

This *Review* article discusses dendritic organometallic catalysis, originating from catalytic moieties present at the peripheries of a dendrimer. The presence of multiple catalytic moieties at the dendrimer peripheries leads to a positive effect in majority of the homogeneous and heterogeneous catalysis, although a negative or a marginal improvement in the catalytic effect with respect to the corresponding monomeric catalyst were also encountered. A number of recent examples that attempt to rationalize the origin of the dendrimer effect in catalysis are discussed. Further a tabular survey is provided by categorizing the dendritic catalysts and their influence on catalysis. Recent studies on the multivalent dendritic catalysts, wherein varied number of catalytic moieties is installed within a given generation, are utilized to emphasize the role of clustering catalytic moieties at the peripheries of the dendrimers in influencing the catalysis.

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Rahul S. Bagul received his BSc (Chemistry) from North Maharashtra University, Jalgaon, and MSc (Organic Chemistry) in 2006 from University of Pune. He joined the PhD programme in the Department of Organic Chemistry, Indian Institute of Science, Bangalore, and received his PhD in 2013 under the supervision of Professor N. Jayaraman. His doctoral work involved studies of endo- and exo-receptor properties of PETIM dendrimers through organometallic catalysis, photo-luminescence and stimuli responsive cross-linking. He is a senior research fellow currently and is working in carbohydrate chemistry in the same group. The author's research interests are in synthesis, organometallic and organocatalysis, supramolecular chemistry and self-assembly.



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Review



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Organometallic catalysis using dendrimers [1] has permitted immensely to understand dendritic structures during last couple of decades. The general features of branches-upon-branches structures originating from a core, well-defined internal voids and precise number of end-groups at the peripheries opened-up importance to interface dendrimers with catalysis, particularly organometallic catalysis [2]. The opportunities to modify the properties of a catalyst are several, important among them is the nature and disposition of the ligand constituting the catalyst. Displaying the catalytic moieties onto dendritic structures attracts an interest in order to identify how such display would modify the properties of the catalyst in a given reaction. Sustained studies of catalysis using dendrimers have shown that each segment in the dendritic structure is a potential site for the installation of the catalytic moiety. Thus, the major segments of the core, branching points and the periphery are principal sites for the installation of catalytic moieties. Each segment provides a modification of the environment around the catalytic moiety at the least. Thus, whereas the catalytic moiety at the core might remain isolated from the bulk environment due to dendritic shell offering the protection, the same at the periphery would experience the most effect of the bulk environment. Whereas, the catalytic moieties present at the branch points would encounter the effect in between. The number of catalytic moieties that can be installed is higher when present at the periphery, in comparison to that at the branch sites or the core. Such possibilities at different segments of the dendritic structures



Fig. 1. Molecular structures of a particular generation of: (a) poly(amido amine) (PAMAM); (b) poly(aryl benzyl ether); (c) poly(propylene imine) (PPI); (d) phosphorous dendrimer; (e) carbosilane dendrimer; (f) poly(propyl ether imine) (PETIM); (g) poly(alkyl aryl ether); (h) polyglycerol and (i) polyhedral oligomeric silsesquioxane (POSS) dendrimer.

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