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VINYLATION REACTIONS OF DICARBOXYLIC ACIDS: CATALYTIC SYSTEMS, MECHANISMS, AND MODERN APPROACHES

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This study presents a comprehensive analysis of the scientific literature on the vinylation of dicarboxylic acids. The principal approaches for the synthesis of vinyl and divinyl esters from dicarboxylic acids are reviewed, with particular emphasis on transvinylation and acetylene-mediated vinylation processes. The composition, catalytic activity, and selectivity of homogeneous and heterogeneous catalytic systems are examined, together with the effects of catalyst nature, reaction temperature, solvent, and reaction time on product yield. Particular attention is given to the relationship between the molecular structure and reactivity of aromatic and aliphatic dicarboxylic acids. The proposed mechanistic pathways of vinylation reactions and the prospects for employing modern nanoscale and supported catalysts are also discussed. Based on the critical analysis of the available literature, promising directions for the development of highly active and selective catalytic systems and for the technological optimization of vinylation processes are identified.

Introduction and Literature Review

Vinylation reactions of dicarboxylic acids represent a promising area of modern organic synthesis and polymer chemistry. The divinyl esters obtained through these processes are

highly reactive compounds and are therefore employed as important monomers in polymerization and copolymerization reactions, as well as in the synthesis of functional materials and various organic compounds. In recent years, considerable attention has been devoted to the development of novel functional and bio-based polymeric materials derived from vinyl ethers [1]. One of the principal approaches to the vinylation of carboxylic acids is the **transvinylation reaction** using vinyl donors, particularly vinyl acetate. In this process, the nature of the catalyst, its acid–base properties, and the reaction conditions have a significant influence on product yield. Recent studies have investigated catalytic systems based on Pd, Ru, Rh, and Ir as alternatives to conventional mercury-based catalysts [2].

Kadidae et al. investigated the transvinylation of hydroxycinnamic acids in the presence of $Pd(OAc)_2$ and demonstrated that the addition of KOH or H_2SO_4 to the catalytic system substantially increased the yield of the corresponding vinyl ethers. These findings indicate that, in addition to the nature of the metal catalyst, the acid–base characteristics of the reaction medium play an important role in determining the efficiency of the process [3]. The catalytic activity of Ru-based Grubbs-type catalysts in transvinylation reactions has also been investigated, with the involvement of metal–vinyl or carbene-type intermediate complexes proposed as part of the reaction pathway [4]. Ir-based catalytic systems have likewise demonstrated the possibility of obtaining bis-vinyl ethers with high selectivity using vinyl acetate, while the underlying catalytic mechanism has been rationalized through DFT calculations [5].

An important alternative approach to the vinylation of dicarboxylic acids is **direct vinylation with acetylene**. In this process, acetylene serves as the source of the vinyl group. In recent studies, increasing attention has been directed toward supported and heterogeneous catalysts as alternatives to homogeneous catalytic systems. In particular, the vinylation of aromatic carboxylic acids with acetylene has been investigated using Zn/SiOC, ZnO/SiOC, and Ni/SiOC catalytic systems, among which Zn/SiOC exhibited comparatively high catalytic activity [6].

Overall, research conducted over the past decade has increasingly focused on the development and optimization of catalytic systems, the design of heterogeneous and nanoscale catalysts, and the elucidation of vinylation mechanisms using quantum-chemical methods. Nevertheless, a comprehensive understanding of the relationship between the molecular structure, electronic properties, and reactivity of dicarboxylic acids remains an important and relevant research problem. Further systematic investigation of these relationships is essential for the rational design of efficient catalytic systems and the development of technologically viable vinylation processes.

Comparative Analysis and Review Findings

The analysis of the literature on the vinylation of dicarboxylic acids demonstrates that the efficiency of vinyl ether synthesis is governed primarily by the nature of the catalytic system, the molecular structure of the substrate, and the technological parameters of the

process. Based on a comparative evaluation of the available studies, vinylation processes can be broadly classified into two major approaches: transvinylation and direct vinylation with acetylene. In transvinylation, vinyl acetate is commonly employed as the principal vinyl donor, enabling high selectivity under relatively mild reaction conditions. However, the requirement for additional reagents and the formation of by-products may reduce the overall atom economy of the process to some extent.

Direct vinylation with acetylene, in contrast, is theoretically a simpler and more atom-economical approach, as it involves the direct transfer of the vinyl group from acetylene to the substrate. A major advantage of this method is the absence of an additional organic vinyl donor. Nevertheless, the high reactivity of acetylene and the need for precise control over the active sites of the catalyst introduce additional technological challenges. In this context, the use of heterogeneous catalysts offers important advantages, particularly with respect to catalyst separation from the reaction mixture, catalyst recovery and reuse, and potential adaptation of the process to continuous operation.

From the perspective of catalyst composition, homogeneous systems based on Pd, Ru, and Ir are distinguished by their high catalytic activity and selectivity. However, the use of expensive metals in some of these systems, together with difficulties associated with catalyst separation from the products and limited opportunities for catalyst recovery and reuse, may restrict their practical application on an industrial scale. Accordingly, supported Zn-based catalysts can be considered an economically and technologically attractive alternative for vinylation processes.

The influence of substrate structure on vinylation reactivity also emerges as an important trend in the literature. In aromatic dicarboxylic acids, the relative positions of the carboxyl groups on the benzene ring affect reactivity through both electronic and steric factors. In aliphatic dicarboxylic acids, the length and conformational characteristics of the hydrocarbon chain separating the carboxyl groups play a significant role. Consequently, under identical catalytic conditions, the yields of divinyl esters obtained from different dicarboxylic acids may differ substantially.

The analyzed data indicate that improving vinylation efficiency requires consideration of the interplay between the active site of the catalyst and the electronic structure of the substrate. The Lewis acidity, electron density, and ability of the catalytic center to activate acetylene directly influence the initial stages of the reaction. The support material may further enhance catalytic performance by controlling the dispersion, surface area, and electronic state of the active metal species.

Furthermore, the application of DFT and other quantum-chemical computational methods in contemporary research provides deeper insight into the mechanisms of vinylation reactions. Analysis of HOMO–LUMO energy gaps, Fukui functions, electron-density distributions, and activation energies makes it possible to predict and compare the reactivity of different substrates. Such an approach provides an important theoretical basis for the

rational planning of experimental synthesis and the development of novel, highly efficient catalytic systems.

Overall, the literature analysis demonstrates that high catalytic activity alone is not a sufficient criterion for determining the practical potential of a catalyst. Catalyst assessment should additionally consider selectivity, metal cost and toxicity, catalyst regeneration capability, support stability, energy consumption, and the environmental sustainability of the overall process. From this perspective, supported Zn-based heterogeneous catalytic systems represent one of the promising directions for the vinylation of dicarboxylic acids with acetylene. Future studies should focus on detailed characterization of catalyst surface structures and active sites, quantum-chemical modeling of the elementary steps of the catalytic cycle, and systematic investigation of catalyst regeneration and long-term stability. Such studies would further enhance both the scientific understanding and the practical relevance of this research direction.

Conclusion

The analysis of scientific literature published over the past decade on the vinylation of dicarboxylic acids demonstrates that this process represents a promising synthetic route for the preparation of divinyl esters. A comparative assessment of transvinylation and direct vinylation with acetylene indicates that the nature of the catalytic system, the molecular structure of the substrate, and the reaction conditions are the principal factors governing process efficiency.

Although homogeneous catalysts based on Pd, Ru, and Ir can provide high catalytic activity and selectivity, their relatively high cost, difficulties associated with catalyst separation from the products, and limited reusability highlight the need for further development of heterogeneous catalytic systems. In this regard, supported Zn-based catalysts represent a promising alternative for acetylene-mediated vinylation owing to their potential advantages in terms of active-site dispersion, catalyst separation, recovery, and regeneration.

The analysis further demonstrates that the molecular structure of dicarboxylic acids has a significant influence on their reactivity in vinylation reactions. Consideration of the electronic and steric characteristics of both aromatic and aliphatic substrates is therefore essential for the targeted optimization of catalytic processes. At the same time, the application of DFT calculations, HOMO–LUMO analysis, and Fukui functions provides valuable opportunities for elucidating vinylation mechanisms and predicting the relative reactivity of substrates.

Future research should focus on the development of highly active and selective heterogeneous catalysts with reduced toxicity and enhanced recyclability, as well as on the identification and characterization of their surface active sites. Particular attention should be devoted to quantum-chemical modeling of the elementary steps of the catalytic cycle and systematic investigation of catalyst regeneration and long-term stability. These approaches can provide a sound scientific basis for the development of environmentally sustainable,

economically viable, and technologically efficient processes for the vinylation of dicarboxylic acids.

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