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Ruthenium-Based Macromolecules as Potential Catalysts in Homogeneous and Heterogeneous Phases for the Utilization of Carbon Dioxide

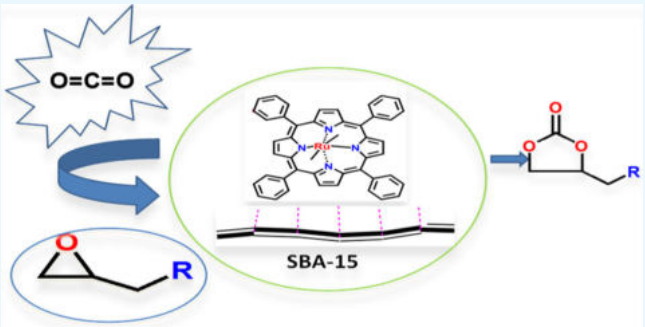
Kaiprathu Anjali,[†] Jayaraj Christopher,[‡] and Ayyamperumal Sakthivel*[,†]

[†]Inorganic Materials & Heterogeneous Catalysis Laboratory, Department of Chemistry, School of Physical Sciences, Central University of Kerala Kasaragod, Sabarmati Building, Tejawini Hills, Kasaragod 671316, India

[‡]Indian Oil Corporation Limited, R&D Centre, Faridabad 121007, India

Supporting Information

ABSTRACT: Ruthenium-containing tetraphenylporphyrin (Ru-TPP) molecule was prepared, and the structural elucidation was confirmed using ^{1}H nuclear magnetic resonance (NMR), CHN, and mass spectral analyses. The incorporation of ruthenium ion into the cavities of the macromolecule was confirmed from the disappearance of the ^{1}H NMR signal, characteristic of the N−H bond (−2.72 ppm in TPP). The CHN and mass spectral analyses of the ligand and metallomacromolecules are consistent with the theoretically calculated values. The homogeneous Ru-TPP macromolecule is grafted on the surface of aminosilane-, diaminosilane-, and iodosilane-functionalized SBA-15 molecular sieves. The successful grafting of Ru-TPP on functionalized mesoporous molecular sieve materials was evident from low-angle powder X-ray diffraction, ^{13}C magic angle spinning NMR, and scanning electron microscopy−energy-dispersive X-ray analyses. The resultant homogeneous and heterogenized Ru-TPP catalysts were used for the utilization of carbon dioxide (CO_2) under moderate reaction conditions. The homogeneous Ru-TPP catalyst showed first-order kinetics with respect to epoxide with the exclusive formation of cyclic carbonate (about 98%) and an activation energy of 16.07 kg/mol, which is much lower than some of the reported catalysts. Ru-TPP grafted on aminosilane- and iodosilane-functionalized materials showed better catalytic activity (above 90% conversion and 83−96% cyclic carbonate selectivity) and reusability for the chosen reaction.



1. INTRODUCTION

CO_2 is an important constituent of air with a typical concentration of ∼400 ppm. The conversion and utilization of CO_2 into gasoline, cyclic carbonates, useful chemicals, and so forth are currently interesting research areas.[1] The International Panel on Climate Change has reported that CO_2 concentrations have increased by 19%,[2] which contributes to climate change via global warming. Consequently, CO_2 is considered the most abundant and cheapest source of carbon that can be utilize for the synthesis of various organic products.[3] During the last three decades, various materials have been used as CO_2 adsorbents, including zeolites, metal organic frameworks, porous carbon, and carbon nanotubes.[4] Another important process employs CO_2 for electrochemical reduction to methanol, formic acid, methane, and other compounds.[5] Similarly, the utilization of CO_2 as a renewable carbon feedstock in the synthesis of cyclic carbonate is an important process as well as growing field of research, both from academic and industrial points of view.[6−18] Cyclic carbonates are important intermediates and building blocks in the synthesis of various fine chemicals, such as carbonates, glycols, carbamates, and pyrimidines, as well as solvents for polymeric resins.[6] They are widely used as aprotic polar solvents, organic synthetic intermediates, and in some biomedical applications.[19] Recent reports have demonstrated the application of cyclic carbonates as versatile etherifying agents for lignin and tannin functionalization, which are the most important and widely available renewable sources of aromatic structures.[20] Reportedly, for the utilization of CO_2, both homogeneous and heterogeneous catalysts require vigorous reaction conditions, such as relatively high pressure, temperature, solvents, and expensive cocatalysts, because of the low reactivity of CO_2.[9−18,21−25] Therefore, researchers are interested in developing efficient catalysts for the utilization of CO_2 by the conversion of epoxide into the corresponding carbonate, under comparable reaction conditions.

It is well known that biological systems convert CO_2 by photosynthesis in the presence of metallomacromolecules. In this regard, various metalloporphyrin molecules have been demonstrated as potential catalysts for several organic

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