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A b s t r a c t

Title	A Novel Strategy for The Synthesis of Porous-Polymer-Supported Ru(II) Complexes and Their Catalytic Applications
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(800 words)

Covalent immobilization of homogeneous catalysts to insoluble polymer supports has received considerable attention in recent years. The heterogenization facilitates the separation of the catalyst from reagents and products, simplifies the efficient recovery of the often-expensive catalysts, and potentially allows the reuse of these catalysts. Unfortunately, the immobilization of chiral catalysts often results in lower activities and enantioselectivities as compared to those observed for their homogeneous counterparts. For this regard, we successfully achieved a new strategy for synthesizing novel porous-polymer-supported chiral Ru(II)-phenyl oxazoline (Ru(II)-pheox) complexes. And, we evaluated their catalytic efficiency in carbene transfer and oxidation reactions.

Chapter 1 describes the main advantages of immobilized catalysts over the homogeneous catalysts. The immobilization strategies and types of polymer-supported catalysts have been also illustrated in this chapter. In addition, a brief summary of the most successful applications of the polymer-supported catalysts over the past ten years was provided.

Chapter 2 provides a novel strategy for the synthesis of porous-polymer-supported Ru(II)-phenyloxazoline complex by using complexation then polymerization technique. The catalytic efficiency of the novel polymeric catalyst were evaluated in inter- and intramolecular cyclopropanation reactions. In case of intermolecular cyclopropanation, the porous catalyst showed excellent reactivity and enantioselectivity compared to the other classical types of polymer-support. A wide variety of terminal olefins with various electronic properties were studied. Interestingly, superior reactivities and excellent enantioselectivities were achieved with various substrates. Impressively, the porous-polymeric-catalyst could be reused more than ten times, even after three months of storage of the used catalyst, without any loss in its catalytic activity or selectivity. In case of intramolecular cyclopropanation, the porous-polymeric catalyst presented excellent reactivity and enantioselectivity not only compared to the other types of polymers but also compared to the homogeneous catalyst analogue. A broad class of *trans*-allylic diazoacetates were effectively cyclopropanated with excellent reactivities and enantioselectivities. The catalyst could be reused at least five times.

Chapter 3 presents a water-soluble chiral Ru(II)-*hm*-pheox complex as a reusable and highly enantioselective catalyst in intramolecular cyclopropanation of *trans*-allylic diazoacetates in a water/ether biphasic medium. A variety of Ru(II)-pheox catalysts with different functional groups were screened and found that the functionality of the ruthenium catalyst with polar protic group is important to furnish the cyclopropanation product in high yield. Different types of *trans*-allylic diazoacetates were investigated and afforded excellent reactivities up to 99% yield and enantioselectivities up to 97% *ee*. The easily separation of the ether-phase, which contains the cyclopropane product, allows the simple reuse of the catalyst in the water-phase at least five times without significant decrease in reactivity or enantioselectivity. To our knowledge, this is the first report of a reusable water-soluble catalyst in intramolecular cyclopropanation reaction.

Chapter 4 explains the use of porous-polymer-supported Ru(II)-*dm*-pheox in the intermolecular N-H insertion of EDA into various primary and secondary amines. The porous polymer-supported Ru(II)-*dm*-pheox was synthesized as previously described in chapter 2. We tested the catalytic activity of the porous-polymer in the N-H insertion of EDA into *N*-methylaniline and found that the polymeric catalyst had ability to quantitatively deliver the α -aminoester product in 15 minute at room temperature. After optimizing the reaction conditions, a wide variety of primary and secondary amines were studied and excellent yields (88->99%) were achieved. The polymeric catalyst was easily recovered by centrifugation and reused at least five times without any decrease in reactivity. Mechanistic studies showed that the N-H insertion product formed via yilde intermediate formation.

Chapter 5 discusses the quinones synthesis via hydrogen peroxide or aerobic oxidations of dihydroxy arenes catalyzed by Ru(II)-*dm*-pheox catalyst or its porous polymeric support. We studied in this chapter the catalytic efficiency of the Ru(II)-*dm*-pheox in the hydrogen peroxide oxidation of various dihydroxy arenes and found that the homogeneous Ru-catalyst had ability to quantitatively deliver the 1,4-quinone products in 5 minute and the 1,2-quinone product in 10 minute to 4 hours. Although the rate of the oxidation by using polymer-supported Ru(II)-*dm*-pheox catalyst was low, The polymeric-catalyst could be readily recovered and recycled at least five times without loss of its catalytic activity. We have also established a new catalytic system from polymer-supported Ru(II)-*dm*-pheox and silica-gel that proved itself as a powerful catalyst in aerobic oxidation of various dihydroxy arenes. The polymer/silica-gel system had ability to be reused several times in aerobic oxidation of various dihydroxy arenes using oxygen balloon or air as oxidant without decrease in yields.

Chapter 6 provides the experimental and analytical data for chapters 2 to 5.

In summary, we have successfully designed and synthesized novel porous polymer-supported Ru(II)-pheox catalysts. The polymeric catalysts showed excellent reactivities and selectivities in carbene transfer and oxidation reactions. The porous-catalysts had ability to be reused several times and stored after reused without loss of its catalytic activity or selectivity. In addition, no significant leaching of the catalysts was detected.