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Ammonium tagged Hoveyda-Grubbs catalysts immobilized on magnetically separable core-shell silica supports for ring-closing metathesis reactions

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ABSTRACT

Ammonium tagged Hoveyda-Grubbs (**Ru-1**) catalyst was immobilized on core-shell structured silica gel bearing a magnetic nano-sized α-Fe_2O_3 core via non-covalent interactions. Core-shell silica gel materials were synthesized using a two-step coating procedure of α-Fe_2O_3 in the presence of cationic (dodecyl trimethyl ammonium chloride, DTMAC) and non-ionic (Synperonic F108) surfactants and tetraethoxysilane (TEOS) as the silica source. Double SiO_2 coated SiO_2(2)@α-Fe_2O_3 supports with a high surface area of 646 m^2/g and pore size/volumes of 2.88 nm/0.393 cm^3 were obtained after removal of template surfactants from silica gel by extraction. Supported catalyst, Ru-1@SiO_2(2)@α-Fe_2O_3, was found to be very active in ring-closing metathesis (RCM) reactions of diethyl diallyl malonate (DEDAM) and various dienes. The catalyst can be easily separated from the reaction mixture with the aid of a magnet and was reusable up to eight times with low Ru leaching levels.

1. Introduction

Olefin metathesis is an efficient method to form new carbon-carbon double bonds in both simple and complex molecular structures [1]. Owing to their functional group tolerance and air/moisture stability, Grubbs type ruthenium catalysts are widely used in several organic, polymer, pharmaceutical and natural product synthesis reactions. In the continuous search for the "perfect" ruthenium olefin metathesis catalyst, several variants of Hoveyda-Grubbs type complexes were developed by several research groups (Scheme 1) [2]. The alternation of ligands in Hoveyda-Grubbs type catalyst to improve the reusability and stability of the catalyst has led the discovery of novel ruthenium catalyst with unique features such as reusability and silica gel affinity [3].

For the last decade, a remarkable number of studies were focused on the development of reusable supported ruthenium catalysts. Several different materials such as; silica gels, polymers, and ionic liquids have been used in the search for the perfect support material for the immobilization of homogeneous ruthenium catalysts [4,5]. These support materials improve the stability and functional group tolerances of homogenous ruthenium counterparts. In addition to above-mentioned features, solid support immobilization offers a great solution for ruthenium recovery problems. Several different strategies were used to immobilize Grubbs type ruthenium catalysts on various support surfaces utilizing covalent linkage via halide ligands, phosphine, alkylidene and N-heterocyclic carbene (NHC) ligands [6].

Ammonium tagged Hoveyda-Grubbs type catalysts have emerged as novel environmental friendly catalysts with high silica gel affinity and improved water compatibility [7] (Scheme 1). The high silica gel affinity of the ammonium tagged ruthenium catalysts allows the synthesis of ruthenium free olefinic products which are useful in pharmaceutical applications with simple filtration through silica gel. Hoveyda-Grubbs type catalysts bearing cationic tagged NHC ligands (Scheme 2, Ru-1) were supported on several lamellar zeolites such as MCM-22, MCM-56 and MCM-36 and used in RCM of citronelle and N,N-diallyltrifluoroacetamide [8]. SBA-15 was used as an alternative support for ammonium tagged Hoveyda-Grubbs type catalysts with high turnover numbers up to 35000 in RCM and cross-metathesis (CM) reactions [9]. Later on, this catalyst system was used in metathesis reactions of cardanol; a renewable source of phenolic compounds, in a continuous flow reactor with a cumulative turn-over number (TON) of 2500 [10]. As a practical application, Ru-1 (Scheme 1) supported on commercial solid materials such as silica gel, alumina, cotton wool, filter paper, iron powder and Pd on carbon and found to catalyze olefin metathesis reactions in excellent yields with minimum ruthenium leaching [11]. In addition to classic support materials, metal-organic frameworks (MOFs) were used to support ammonium tagged Hoveyda-Grubbs catalysts (Scheme 1, Ru-1, Ru-2, Ru-4) and proved to be held the complex inside the MOF structure by only noncovalent forces [12].

The separation and recovery of the catalyst are crucial for the development of reusable catalyst systems and sustainable catalytic processes. The separation difficulties can be overcome by the magnetic recovery of the catalyst. Magnetic recovery of catalysts is usually achieved by integrating magnetic nanoparticles such as α-Fe_2O_3, Fe_3O_4 and various metal oxides on the support structure [13]. Commercially

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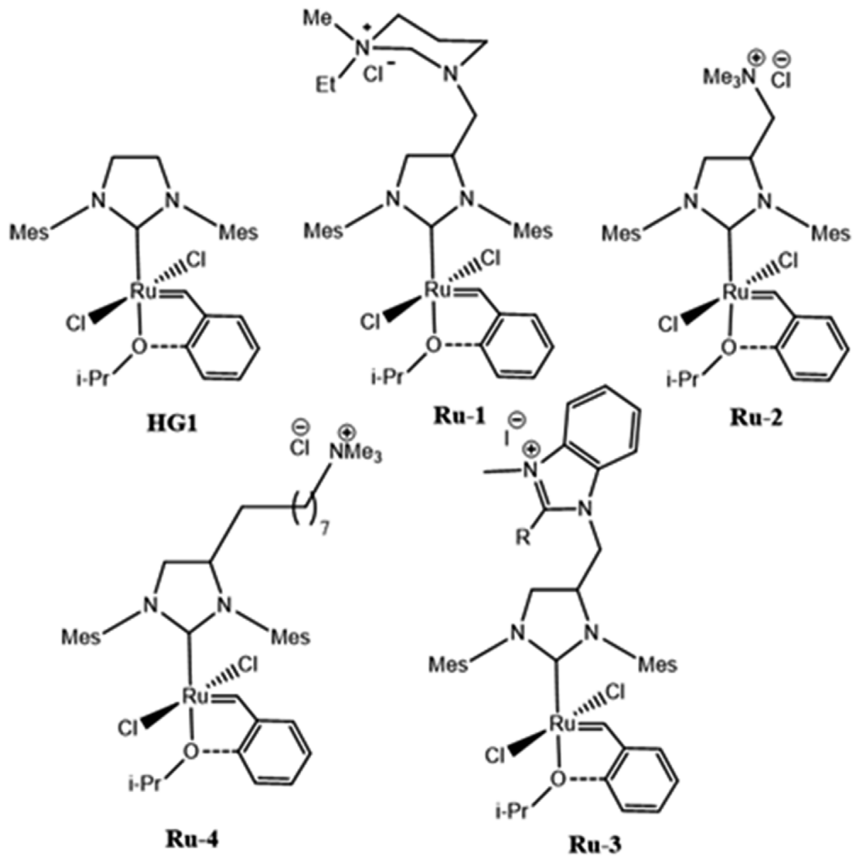
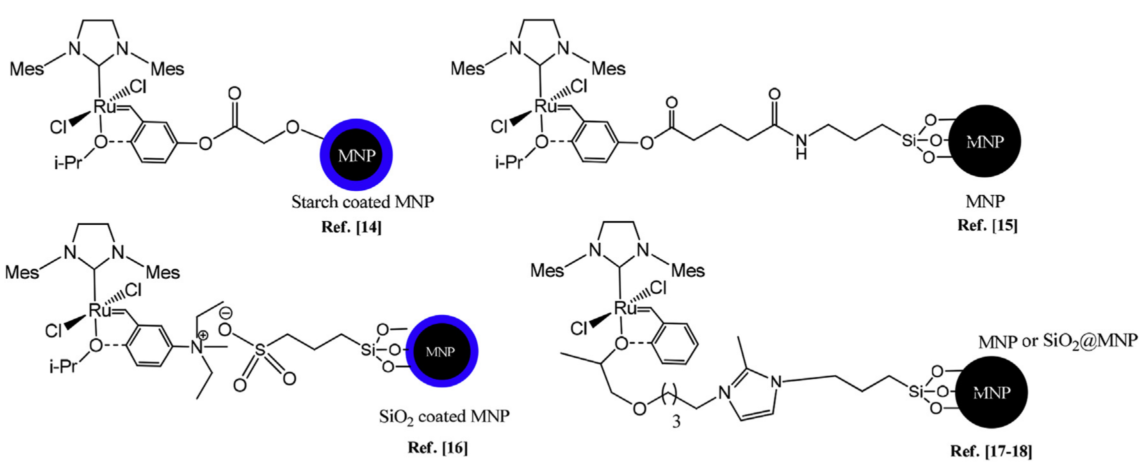


Scheme 1. Olefin Metathesis Catalysts.



Scheme 2. Magnetically separable ruthenium metathesis catalysts.

available starched coated magnetic nanoparticles (100 nm) are covalently modified by ortho-isopropoxy styrene groups. Grubbs 2nd generation catalyst (G2) was supported on the modified magnetic particles and used in metathesis reactions of methyl oleate [14] (Scheme 2). Another covalent immobilization strategy was developed by Jiang et al. utilizing the modified iron oxide particles with 3-aminopropyltriethoxysilane groups. Subsequent modification of amine groups with isopropoxy styrene derivatives, followed by immobilization of Grubbs 1st generation catalyst (G1) has led to the formation of magnetically separable Hoveyda-Grubbs type catalysts [15].

Magnetic α-Fe_2O_3 was coated with a thin layer of silica containing sulfoxide and Hoveyda-Grubbs type complexes bearing quaternary ammonium groups were immobilized to the magnetic support (Scheme 2) through electrostatic attraction [16]. Lee et al. covalently modified magnetic Fe_3O_4 particles using isopropoxy styrene groups bearing siloxane-based imidazole salt linkers. Magnetically separable Hoveyda-Grubbs type catalyst was achieved by supporting the G2 catalyst on the support. The catalyst can be used on RCM reactions up to seven times with minimum catalyst leaching [17,18].

To the best of our knowledge, up to date, only five examples of magnetically separable ruthenium metathesis catalysts were reported in the literature. Several different immobilization strategies, as well as various support materials, were employed in the design of magnetically separable ruthenium catalysts. Considering the recent studies on supported ruthenium catalysts, ammonium tagged Hoveyda-Grubbs complexes/silica gel based support systems performs better in various olefin