Journal of Molecular Catalysis A: Chemical 372 (2013) 35–43

Contents lists available at SciVerse ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

Grubbs-type catalysts immobilized on SBA-15: A novel heterogeneous catalyst for olefin metathesis

Huan Zhang, Ying Li, Songxue Shao, Haihong Wu*, Peng Wu*

Shanghai Key Laboratory of Green Chemistry and Chemical Processes, Department of Chemistry, East China Normal University, 3663 North Zhongshan Road, Shanghai 200062, China

ARTICLE INFO

Article history:
Received 15 September 2012
Received in revised form 18 January 2013
Accepted 19 January 2013
Available online 18 February 2013

Keywords:
Heterogeneous catalysis
Grubbs-type catalyst
SBA-15 mesoporous silica
Ring-closing olefin metathesis
Immobilization

ABSTRACT

A series of novel heterogeneous olefin metathesis catalysts have been developed by immobilizing Ru species on SBA-15 mesoporous silica with tunable ordered pores and different textural properties. Various techniques such as X-ray diffraction, N_2 adsorption–desorption, high resolution transmission electron microscopy have been used to characterize the physicochemical properties of the catalysts. The catalytic activity of thus prepared Ru-based catalysts has been studied in ring closing metathesis (RCM) and other metathesis reactions. Among these immobilized catalysts, the SBA-15 support with the largest pore size gives rise to the highest catalytic activity because the large pores are benefit for the diffusion of reactants and products. The immobilized Ru catalysts prove to be reusable in RCM reactions. Their catalytic activity is closely related to the confinement effect and high hydrophobicity of SBA-15 mesopores.

1. Introduction

Olefin metathesis, a transition metal-catalyzed interexchange reaction of alkylidene units between two substituted alkenes, is an effective and useful method for constructing carbon–carbon double bonds, which attracts growing research attentions in organic synthesis in recent years [1]. It opens up new industrial routes to synthesize valuable petrochemicals, polymers, oleochemicals and specialty chemicals. As remarkable olefin metathesis catalysts, ruthenium-based carbene complexes developed by Grubbs [2] have significantly broadened the scope of the olefin metathesis reaction (Scheme 1). Lately, several modified Grubbs-type catalysts have also been developed and intensively studied [3].

Despite of the successes to ring construction, there is still a large room to improve this general approach in terms of scope, convenience and generality. Most of homogeneous Grubbs-type catalysts are hard to be reused and recycled after reactions. Furthermore, the homogeneous systems suffer the difficulty of removing residual ruthenium byproducts from the reaction products [4]. Nowadays, the use of environmentally friendly heterogeneous catalysts has become an important research target for green chemistry. Immobilizing homogeneous catalytic species on solid supports and scavenging residual catalysts are the most effective ways to solve the problems. Several immobilized Grubbs-type catalysts have been reported by using polymer supports including vinyl polystyrene [5], polyethylene glycol [6], PEGA-NH_2 resin [7], Poly (fluoroalkyl acrylate) [8], PolyHIPE [9], and so on [10]. The polymers possess usually a relatively low thermal stability, making the recovered catalysts less active in reuse.

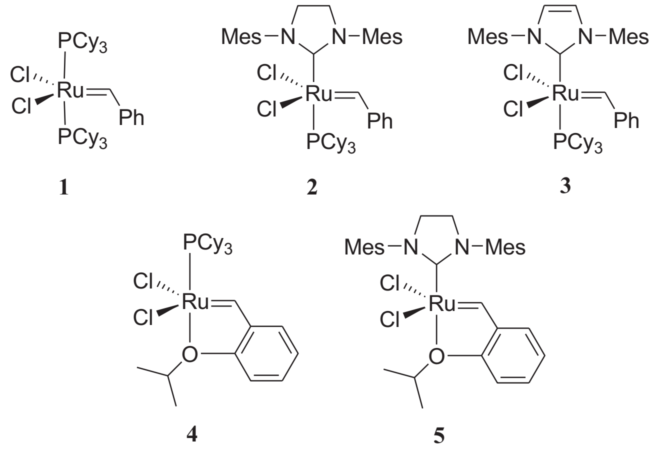
Since the discovery of the M41S family [11], ordered mesoporous silica materials are widely investigated because of their high surface area, large adsorption capacity, diverse morphologies and tunable mesopores [12]. Thereafter, these ordered mesoporous silica materials such as MCM-41 [13], siliceous mesocellular foam [14], etc., are used as supports for the Grubbs-type catalysts. Among these materials, SBA-15, a kind of important hexagonal mesoporous silicas [15], has been developed and investigated in various applications as it has larger pore size, thicker silica walls and higher hydrothermal stability [16]. Using these mesoporous materials as supports, several generations immobilized Grubbs catalysts have been reported [17]. In 2005, Shi and coworkers anchored first generation of Grubbs catalyst on the inner pore surface of SBA-15 through the *N*-heterocyclic carbene ligands, which effectively prevented the decomposition of the catalytic species. SBA-15-supported catalysts thus prepared achieved a durable catalytic activity [17a].

The supported catalysts prepared from the second generation Grubbs complex gave much higher reaction rates than those from the first generation one. A second generation Hoveyda–Grubbs catalyst was once immobilized on silica without any linkers but simply by mixing the Ru complex with silica in a suspension [18]. Hoveyda–Grubbs-type complexes were also covalently bonded to a silica matrix by sol-gel processes. They were shown to be superior

---

* Corresponding authors. Tel.: +86 21 62238510; fax: +86 21 62238510.
E-mail addresses: hhwu@chem.ecnu.edu.cn (H. Wu), pwu@chem.ecnu.edu.cn (P. Wu).

1381-1169/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.molcata.2013.01.034



Scheme 1. Grubbs-type catalysts.

to those prepared through anchoring the complexes to commercial silica or meso-structured MCM-41 in the ring-closing metathesis reactions of dienes (II) and enyne (IV) [19].

However, most of supported catalysts exhibit a lower activity in comparison to homogeneous counterparts and suffer substantial leaching of the ruthenium species. The supported catalytic species should have suitable interactions with the surface, whether functionalized or not, in order to obtain a desired catalytic activity [20]. Therefore, a proper understanding of the nature on inorganic support surface would provide deep insights into the activity of the supported metathesis catalysts. Polarz et al. proved that the covering of surface silanols may stabilize the Grubbs catalyst [17c]. Recently, Fontaine and coworkers further demonstrated the pore surface functionalities of mesoporous SBA-15 silica influenced the stability of first generation Grubbs catalyst. The presence of surface silanols significantly decreases the longevity of the ring-closing metathesis catalyst, whereas total passivation of the surface with trimethylsilyl groups prevents the catalyst from deactivating, but slows down the reaction rate [17d].

Compared to organic polymers, mesoporous silica material is a common support for immobilization due to its higher thermal and chemical stability. It has already been discussed that a confining reaction field affects intermolecular equilibrium reactions very strongly [17c]. In this context, we design new method for immobilization and use SBA-15 with different pore sizes as supports for the heterogenization of the first-generation or second-generation Grubbs catalyst. The surface hydrophilicity/hydrophobicity of SBA-15 with variable pore sizes is quite different because of the various synthesis conditions. It will allow a different loading of these large catalytic species throughout the matrix, which results in different catalytic conversions of bulky organic reactants.

In this study, with purpose to prepare active and stable heterogeneous Grubbs catalysts, we synthesized a series of SBA-15 ordered mesoporous silica materials with variable pore sizes, and then immobilized the Grubbs-type catalysts on them. We prepared a series of new supported catalysts and studied the catalytic activity of them in ring-closing metathesis (RCM), self-metathesis and cross-metathesis (CM) reactions.

2. Experimental

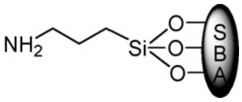
2.1. General

All reagents were commercially available (Aldrich) and were directly used without further purification. All reactions were carried out in Argonaut advantage series^{TM} 2410 personal screening synthesizer. All non-aqueous reactions were performed under an argon atmosphere. ^1H spectra were acquired on a Bruker DRX500 spectrometer at 500 MHz in $CDCl_3$. TMS was used as an internal standard for ^1H spectra. Flash column chromatography was performed using silica gel 60 (230–400 mesh). The X-ray diffraction (XRD) patterns were collected on a Bruker D8 ADVANCE instrument using Cu-K_α radiation ($\lambda = 1.5418$ Å) at 40 kV and 40 mA. Nitrogen adsorption–desorption isotherms were recorded on a Quancachrome Autosorb-3B instrument. The specific surface areas were evaluated using Brunauer–Emmett–Teller (BET) method. The TEM images were recorded using a JEOL-JEM-2010 microscope. IR analyses were obtained with Nicolet NEXUS 670 infrared spectrometer. N elemental analyses were performed on an Elementar VarioEL III CHN elemental analyzer. The bulk loading amount of Ru was determined by ICP (Thermo Electron Corporation IRIS Intrepid II XSP).

2.2. Synthesis of SBA-15 mesoporous materials in different conditions

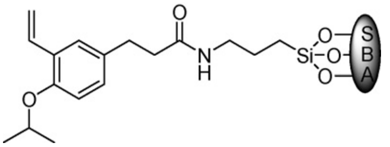
Four kinds of SBA-15 mesoporous materials with different pore sizes were synthesized according to the literatures [15,21]. Both the gel compositions and the condensation temperature were varied changed in order to change pore size or surface. In a typical synthesis, copolymer surfactant P123 was dissolved in deionized water and 2 M HCl solution, followed by the addition of TEOS. Four weight ratios of P123/H_2O/HCl/TEOS actually used in gram were 8.0/72/288/20.4, 6.0/45.2/180/12.3, 6.24/45/180/12.8 and 6.0/187.5/112.5/16.8. The four gels were first stirred at 35 °C for 24 h, and then autoclaved for further condensation for 24 h at 60 °C,100 °C,130 °C and 180 °C, respectively. The products were collected by filtration, dried and calcined at 550 °C for 6 h to remove the surfactant. The samples were denoted as SBA-15-*n* (*n* = a, b, c and d).

2.3. Synthesis of amino-functionalized SBA-15 mesoporous materials (**1a**–**1d**)



SBA-15-a (2.0 g) mesoporous materials were evacuated at 90 °C for 4 h in a three-necked flask, into which dry toluene (60 mL) and 3-aminopropyl triethoxysilane (0.9 g, 4 mmol) were added through a syringe. The mixture was then refluxed at 110 °C for 24 h. After cooling to room temperature, the mixture was filtrated and washed repeatedly with toluene, ethanol and acetone in turns to afford **1a** as a light yellow solid 2.2 g. **1b**–**1d** were obtained by the same method.

2.4. Immobilization of Hoveyda-type ligand on SBA-15 (**6a**–**6d**)



To a solution of 3-(3-vinyl-4-isopropoxyphenyl) propionic Acid **5** (0.80 g, 3.42 mmol) in 50 mL of DMF was added DCC (0.78 g, 3.76 mmol), DMAP (0.125 g, 1.03 mmol) and TsOH (65.0 mg, 0.342 mmol). This solution was stirred at room temperature for 1 h and then amino-functionalized SBA-15-a mesoporous materials **1a** (800 mg) were added in one portion. The mixture was stirred at 70 °C for 72 h. The resulting suspension was filtered and washed repeatedly with CH_2Cl_2, DMF and acetone in turns to afford **6a** as a yellow solid 0.96 g. **6b**–**6d** were obtained by the same method.