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Short Communication

Ruthenium metathesis catalyst bearing chelating carboxylate ligand immobilized on mesoporous molecular sieve SBA-15

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ABSTRACT

Ruthenium complex **3b** bearing chelating carboxylate ligand was immobilized on mesoporous molecular sieve SBA-15 via cleavage of carboxylate by fluorocarboxylic acid groups introduced on the support surface. The hybrid olefin metathesis catalyst Ru/L/SBA-15, prepared straightforward without use of silver salts, exhibited high activity and selectivity in model metathesis reactions and low ruthenium leaching.

1. Introduction

Olefin metathesis became standard tool in organic synthesis [1]. However, it is still a domain of laboratory applications. Only few examples of industrial applications of olefin metathesis are known. The main reason of this is contamination of products by ruthenium catalyst residues, which is difficult (expensive) to remove. Especially in production of chemical specialties (biologically active compounds, pharmaceuticals, and special polymers) low level of Ru in product is required [2]. The second reason is the cost of catalysts, which normally cannot be reused. One of the solutions of these drawbacks is catalyst immobilization on a solid support. In recent years a lot of work was done to immobilize ruthenium olefin metathesis catalysts [3–5].

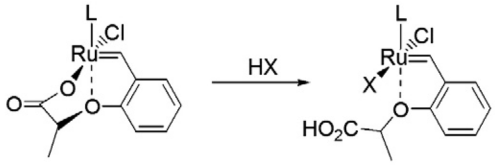
Immobilization of Grubbs (**1a**, **1b**) and Hoveyda–Grubbs alkylidene complexes (**2a**–**2c**, Fig. 1) on solid supports promises new hybrid metathesis catalysts with important advantages: high activity and selectivity, easy separation of catalyst from reaction products, and possibility of catalyst recovery and reusing.

The main strategy for the immobilization is a ligand exchange between Ru complex and the support surface modified with appropriate functional groups. Fundamentally, (i) the exchange of anionic ligands [6–11], (ii) attachment through neutral ligands (NHC [12–14] or phosphanes [15–17]), and (iii) attachment through alkylidene moiety [18–22] can be employed. Immobilization of Hoveyda–Grubbs type catalyst (**2a**–**2c**) by exchange of Cl ligands for carboxylate ones bound to the siliceous support led to the hybrid catalysts active in several type of metathesis reaction, reusable and exhibiting very low Ru leaching [10,23]. However, the Cl ligand exchange requires the application of silver carboxylates [10,24,25], which complicates the catalyst synthesis (especially by necessity of removing of AgCl formed).

Recently ruthenium complex with chelating carboxylate ligand **3a** was reported [26]. Although **3a** is inactive in olefin metathesis it can be straightforward transformed to the highly active form (e.g. **4a** or **4b**) by cleavage of carboxylate protection by various organic and inorganic acids HX (Scheme 1). Employing acids connected to solid supports opens a way for immobilization of **3a** in a straightforward way without using silver salts [27].

Mesoporous molecular sieves [28] with their unique properties such as high surface area, narrow pore size distribution, and thermal and mechanical stability represent advanced supports for transition metal catalysts including metathesis ones [15, 17, 23, 29–32].

In this contribution we report on a new way of immobilization of Hoveyda–Grubbs type metathesis catalyst via anionic ligand exchange using the straightforward reaction of complex **3b** – an iodide analog



3a

4a: HX = HCl
4b: HX = $C_9H_{18}CO_2H$

Scheme 1. Ruthenium carboxylate complex **3a** and its carboxylate opening concept.

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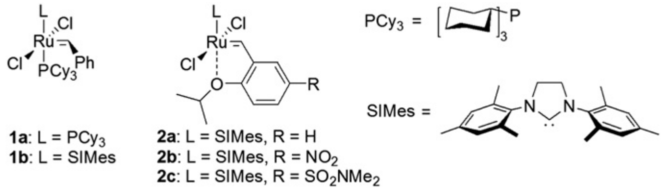

Fig. 1. Grubbs (**1a**, **1b**) and Hoveyda–Grubbs (**2a**–**2c**) olefin metathesis catalysts.

of **3a** – with fluorocarboxylic acid groups on the surface of the mesoporous molecular sieve SBA-15.

2. Experiment

2.1. Materials

Solvents dried by conventional methods were used. Substrates and other chemicals were used as obtained and/or after passing through a column with activated alumina. For details see Appendix A. Mesoporous molecular sieves SBA-15 were prepared by hydrothermal synthesis according to the literature [33]. Linker (L) $(EtO)_3Si(CH_2)_3N(H)C(O)(CF_2)_3COOH$ was synthesized according to the previously published procedure [34].

2.1.1. Modification of SBA-15 with $(EtO)_3Si(CH_2)_3N(H)C(O)(CF_2)_3COOH$

6.5 mL of THF was added to 442 mg of SBA-15 (SBA-15 used was predried in vacuum at 300 °C for 3 h) in a Schlenk tube, then 423 mg of $(EtO)_3Si(CH_2)_3N(H)C(O)(CF_2)_3COOH$ dissolved in 2 mL of THF was added, and the mixture was stirred for 19 h at room temperature. The product was 5 times washed under argon atmosphere with 5 mL of THF and finally the rest of THF was removed by drying of the product in vacuum at room temperature. Four hundred fifty-five milligrams of modified SBA-15 (L/SBA-15) was prepared and stored under argon atmosphere. IR (KBr): $\nu = 3430$, 2981, 2918, 2849, 1770, 1706, 1548 cm^{-1}.

2.1.2. Synthesis of 3b (M = 711.6 g/mol)

664.0 mg (4.0 mmol) of KI was added to the solution of **3a** (124.0 mg, 0.2 mmol) in 6 mL of acetone. Mixture was stirred for 30 min and inorganic salts were filtered. Acetone was evaporated; the residue was dissolved in 4 mL of dichloromethane and passed through a short column of silica. **3b** retained in silica column was washed out with acetone. Then acetone was evaporated, and the residue was dissolved in 4 mL of dichloromethane and passed through a short column of Celite. Two milliliters of ethyl acetate was added to the solution and evaporation of solvent afforded **3b** as a green solid (138.0 mg, 97%). IR (film from CH_2Cl_2): $\nu = 2918$, 1661, 1482, 1268 cm^{-1}; $C_{31}H_{35}IN_2O_3Ru$ (711.61): found C 52.44, H 5.00, I 17.36, N 3.75; calcd. C 52.32, H 4.96, I 17.83, N 3.94; ^1H NMR (600 MHz, $CDCl_3$): $\delta = 15.89$ (s, 1H, Ru = C*H*), 7.60–7.00 (multiplet, 8H, aromat. C*H*, mes. C*H*,), 4.79 (q, 1H, –O–C*H*–CH_3), 4.21 (s, 4H, imidazolidine C*H*$_2$), 2.43 (s, 6H, mes.-*p*-C*H*$_3$), 2.39 (s, 12H, mes. -*o*-C*H*$_3$), 1.2 (d, 3H, –O–CH–C*H*$_3$) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 211.9$, 181.3, 154.4, 146.6, 139.2, 130.3, 129.6, 129.5, 126.6, 122.4, 119.0, 83.9, 30.9, 21.1, 19.2, 18.9 ppm.

2.1.3. Preparation of hybrid catalyst Ru/L/SBA-15

355.8 mg of L/SBA-15 was suspended in 5 mL of dry dichloromethane and 1.7 mL of solution of **3b** ($c_{Ru} = 1680$ mg/L Ru, in CH_2Cl_2) was added. The suspension was stirred at room temperature for 2 h. The product was washed 2 times with 5 mL of toluene and 10 times with 5 mL of dichloromethane under argon atmosphere. The rest of the solvent was removed by drying Ru/L/SBA-15 in vacuum at room temperature. Light green Ru/L/SBA-15 was stored in a Schlenk tube at 10 °C under argon atmosphere.

2.2. Techniques

Textural parameters of SBA-15 and L/SBA-15 were determined from nitrogen adsorption isotherms at −196 °C recorded on a Micromeritics ASAP 2020 instrument. The content of N in L/SBA-15 was determined by elemental analysis using Flash EA2000 CHN/O automatic elemental analyzer (Thermo Scientific). The Ru content was determined by ICP-MS (Institute of Analytical Chemistry of the Institute of Chemical Technology, Prague). NMR spectra were recorded on a Varian Mercury 300 and Varian VNMRS 600 MHz spectrometer. Chemical shifts (δ, ppm) are given relative to the solvents signals.

All manipulations with catalysts as well as catalytic experiments were carried out under argon atmosphere using standard Schlenk tube technique. Catalytic reactions were performed in batch reactors equipped with magnetic stirrers. The reaction progress was followed by GC (a high-resolution gas chromatograph Agilent 6890 with DB-5 column and FID detector). The individual products were identified by GC/MS (ThermoFinnigan, FOCUS DSQ II Single Quadrupole). For details about metathesis experiments see Appendix A.

3. Results and discussion

3.1. Catalyst preparation

SBA-15 modified by linker (L/SBA-15) was prepared by the surface modification of mesoporous molecular sieves SBA-15 (surface area $S_{BET} = 610\ m^2/g$, void volume $V = 1.67\ cm^3/g$, pore diameter $d = 11.1$ nm) with $(EtO)_3Si(CH_2)_3N(H)C(O)(CF_2)_3COOH$ linker molecule (L). The content of N in L/SBA-15 was 0.33 wt% according to the elemental analysis. The analysis of nitrogen adsorption isotherms of L/SBA-15 and parent SBA-15 confirmed the mesoporous character and regular architecture being preserved during the modification (see supplementary data Fig. S1a). Certain decrease of the surface area S_{BET} and void volume V associated with the modification was observed (for L/SBA-15 S_{BET} was 570 m^2/g, and V was 1.42 cm^3/g). Average pore size diameter decreased from 11.1 nm for parent SBA-15 to 9.6 nm for L/SBA-15 preserving narrow pore size distribution (see supplementary data Fig. S1b). It is assumed that textural characteristics of hybrid catalyst Ru/L/SBA-15 (values S_{BET}, V and d) are practically the same as those for L/SBA-15 due to the low content of immobilized Ru species (0.27 wt%, vide infra).

Although the chloride-containing carboxylate **3a** could also be used for immobilization on SBA-15, we were afraid that the known ionic ligand exchange [35] could lead to high ruthenium leaching in this case. Recently it was shown that simply exchanging chloride to iodide in ruthenium carboxylate analog of **3a** can solve this issue [36].

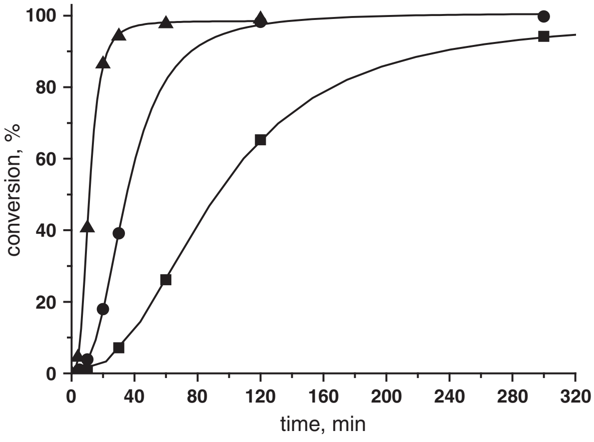

Fig. 2. Conversion curves for RCM of **5** over Ru/L/SBA-15 at 30 °C (■), 40 °C (●) and 60 °C (▲). **5**:Ru = 1500, starting concentration of **5** = 0.15 mol/L, toluene.