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METATHESIS OF CARDANOL OVER AMMONIUM TAGGED HOVEYDA-GRUBBS TYPE CATALYST SUPPORTED ON SBA-15

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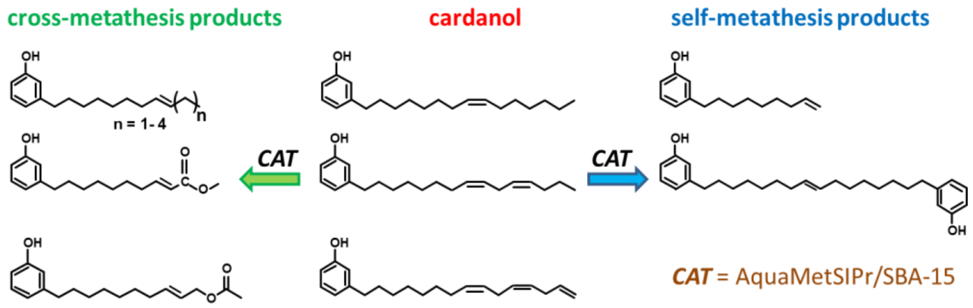
Graphical abstract



Highlights

Ammonium tagged Hoveyda-Grubbs catalyst on SBA-15 was effective in cardanol metathesis.

The catalyst was also used in cross-metathesis with alkenes and unsaturated esters.

The Ru leaching was low and the catalyst was used in continuous flow reactor.

Abstract

Cardanol (a mixture of phenols with C_{15} aliphatic unsaturated chain in *meta* position, manufactured from cashew nut shell liquids) is an abundant and till now practically waste natural material. An important way leading to its utilization as a renewable source of valuable phenolic compounds is represented by olefin metathesis.

Quaternary ammonium tagged Ru complex of Hoveyda-Grubbs type immobilized on SBA-15 mesoporous molecular sieve by non-covalent interactions was proved as a very efficient catalyst for cardanol metathesis under mild conditions (35°C, toluene, 0.1 mol% of catalyst). The catalyst was used also in cross-metathesis of cardanol with alkenes (1-hexene, 1-heptene, 3-hexene, 4-octene) and unsaturated esters (methyl acrylate, 1,4-diacetoxybutene-2) under high yields of cross-metathesis products. The catalysts exhibited low leaching (from 0.2 ppm to 2.9 ppm Ru in products) and can be used in a continuous flow reactor (cumulative TON = 2500).

Keywords: cardanol, olefin metathesis, Hoveyda-Grubbs type catalyst, immobilized catalyst, SBA-15, flow chemistry.

1. Introduction

Cardanol is an important natural product received from cashew nut shell liquid (CNSL)[1,2]. Cashew nut tree (*Anacardium occidentale* L.) is growing in tropical regions (Brazil, Vietnam, Nigeria, India, Cote d’Ivoire) and the world cashew nut crop is more than 3 millions tons per year[1]. Cashew nut shell (about 25% of weight) is normally discarded as a waste. CNSL is produced from nut shells either by solvent extraction or roasting process [3]. Solvent extracted CNLS contains mainly anacardic acid, CNSL from roasting process is rich in cardanol (at high temperature anacardic acid decarboxylates). Cardanol then is obtained by vacuum distillation as a pale yellow viscous liquid and contained a small amount of cardol (Fig. 1). Cardanol itself is a mixture of four *m*-substituted phenols with C15 aliphatic chains of different degree of unsaturation (3,2,1,0 isolated C=C bonds in chain). Similar mixture of resorcin analogues is called cardol. The composition of cardanol varies in some extent and depends on cashew nut origin and method of CNSL extraction.

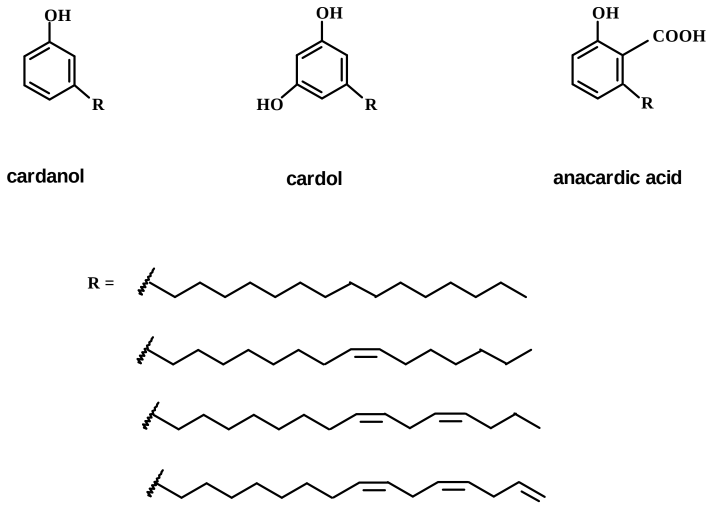


Fig. 1. Main constituents of CNSL.

Till recently cardanol has been used for production of resins and polymer materials. In last decade, its importance as a renewable source of phenolic compounds was recognized and new chemical transformations leading to valuable products have been studied [1,2]. In addition to cardanol hydrogenation, epoxidation, and carbonylation, olefin metathesis has been investigated especially for synthesis of new fine chemicals [4-10]. Among other important products, 3-(non-8-enyl)phenol prepared by cardanol ethenolysis [9] has attracted attention as a precursor molecule for environmental friendly detergents [2].

Metathesis of cardanol proceeds smoothly with Grubbs-, and Hoveyda-Grubbs type Ru catalysts under mild conditions. Protection of phenol OH group is not necessary. However, relatively high amounts of Ru catalysts were used (usually 1 mol % , in some case even 5 mol% [6], in the case of cardanol ethenolysis [9] exceptionally 0.05 mol % of Ru catalyst was used). It is a result of low catalyst stability under conditions applied (catalyst decomposition by reaction with cardanol and impurities in it, inherent catalyst instability). Another problem is connected with homogeneous character of the reaction, i.e. separation of catalyst residues from reaction mixture. This may be solved by immobilization of Ru catalysts on solid supports. Mesoporous molecular sieves (e.g. SBA-15) and two-dimensional zeolites have been proved as advantageous support for immobilization of originally homogeneous catalysts [11,12]. Grubbs second generation catalyst and Hoveyda-Grubbs type Zhan 1B catalyst immobilized on SBA-15 were successfully tested in cardanol metathesis and cardanol cross-metathesis with ethylene and diacetoxybutene [13]. Cardanol was used without special purification and high conversions were achieved under mild conditions (batch reactor, toluene, 35-60°C, 1-2 mol% of catalyst, 2h of reaction time). Nevertheless, with regards to cardanol properties, a low possibility of its further purification, and the desirability of scaling up this process, searching for more efficient and stable catalysts is still necessary.

Recently, Hoveyda-Grubbs type catalysts with ammonium tags were developed and immobilized on SBA-15 by non-covalent interactions [14,15]. These catalysts showed excellent effectivity in metathesis reaction of various substrates, and especially the catalyst with diisopropylphenyl substituents on NHC ligand **1** (Fig.2) exhibited high robustness allowing flow reactor application.

The goal of this contribution is the investigation of the Hoveyda-Grubbs type catalysts with ammonium tags immobilized on the SBA-15 in cardanol metathesis and cross-metathesis with various co-substrates. We followed activity and selectivity of these catalysts under both batch and flow conditions. According to our best knowledge, cardanol metathesis in flow conditions has not been reported till now.

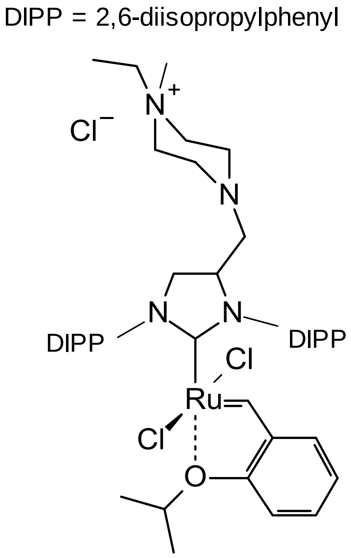


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Fig. 2. Catalyst **1** (AquaMet SIPr).

2. Materials and methods

2.1. Materials

Purely siliceous SBA-15 mesoporous molecular sieve (particle size about 1μm) was synthesized as described elsewhere [16] using a tetraethoxysilane (TEOS; 98%, Aldrich) as a silica source and triblock copolymer Pluronic P123 ($EO_{20}PO_{70}EO_{20}$; BASF) as a structure-directing agent. Catalyst AquaMet SIPr (**1**) was purchased from Apeiron Synthesis S.A. (Poland). Toluene (for HPLC, HiPerSolv Chromanorm, VWR Prolabo Chemicals) and dichloromethane (for HPLC, LachNer, Czech Rep.) were purified using a Pure Solv PS-MD-7 Solvent Purification System (Innovative Technology, Amesbury, MA). Toluene was stored over molecular sieves 4A under Ar. Dichloromethane was degassed and stored in vacuo in dark. 1-Hexene (Fluka, purum), 1-heptene (Fluka, purum), cis-3-hexene (Alfa Aesar), trans-4-octene (Aldrich) were purified by metallic Na, cis-1,4-diacetoxy-2-butene (96%, Alfa Aesar), methyl acrylate (99%, Aldrich) and nonane (99%, Sigma-Algrich) were dried by molecular sieve (Fluka). Cardanol was purchased from Shanghai Boyle Chemical Co., Ltd. China, stored in cold and dark and used without further purification.

2.2. Catalyst preparation

About 1 g of SBA-15 was dried in a Schlenk tube in vacuo at 300°C for 3 h. Then 10-20 mL dichloromethane and calculated amount of **1** were added under Ar. After 30 min stirring the solid phase turned to slightly green and the supernatant became colorless. The supernatant was removed by filtration and the solid phase was washed 3 times by 10 mL dichloromethane. Finally, the solid catalyst was dried in vacuo at room temperature. Catalysts containing 0.09, 0.5, and 1.0 wt% of Ru [**1**/SBA-15 (0.09), **1**/SBA-15 (0.5), and **1**/SBA-15 (1.0)] have been prepared.

N_2 adsorption isotherms (77K, ASAP 2020, Micromeritics) reveal that mesoporous character and narrow pore size distribution of SBA-15 support were preserved in the catalyst (see Figure S1 and S2 in Supplementary material). The comparison of textural parameters of SBA-15 and **1**/SBA-15 (1.0) is given in Table 1. Due to the low Ru concentration (0.07 Ru/nm^2) the decrease in void volume is small and in average pore diameter practically negligible. It is in accord with previous findings [14].

Table 1. Textural parameters of parent support and **1**/SBA-15 (1.0) catalyst.

	S_{BET} (m^2/g)	V (cm^3/g)	D (nm)
SBA-15	864	1.10	5.6
1/SBA-15 (1.0)	699	0.99	5.5

S_{BET} = BET surface area, V = void volume, D = average pore diameter.

2.3.Metathesis experiments and product analysis

The metathesis in batch reactors were carried out under Ar using standard Schlenk technique. Cardanol (together with a co-substrate in case of cross-metathesis) was added to the catalyst suspension in toluene under stirring (800 rpm). The samples of reaction mixture were collected at given reaction times, the catalyst was removed by centrifugation and samples were analyzed by GC, GC-MS and HPLC-MS.

The flow experiments were carried out on a bench-top continuous-flow reactor X-cube (Thales Nano Inc., Budapest, Hungary). Catalyst (about 50 mg) was placed into the cartridge - reactor in an atmosbag under Ar. The toluene solution of cardanol, co-substrate (if any) and nonane (GC internal standard) was pumped from the stock Schlenk tube to the reactor heated to the required temperature. Flow rate was 0.1 mL/min. The liquid on the outlet was collected and analyzed by GC.

A high resolution gas chromatograph Agilent 6890 with a DB-5 column (length: 50 m, inner diameter: 320 μm, stationary phase thickness: 1 μm), equipped with a 7683 Automatic Liquid Sampler and a FID detector was used for product analysis. Temperature parameters: inlet temperature 250°C, detector temperature 250°C, temperature program 100°C (hold 5 min), 10°C/min to 150°C, 20°C/min to 200°C (hold 3 min), 30°C/min to 290°C (hold 10 min), 30°C/min to 325°C (hold 10 min), 20°C/min to 350°C. Flow gas: helium, initial pressure: 150kPa, constant flow 2.8 ml/min. Sample volume was 1 μl, split ratio 25:1. n-Nonane was used as an internal standard. Individual products were identified by GC–MS (ThermoFinnigan, FOCUS DSQ II single Quadrupole) and HPLC–MS.

HPLC-MS analyses were performed using a Waters 1525μ binary HPLC pump connected to a Waters 2487 dual λ absorbance UV detector and a Quattro Premiere XE tandem quadrupole mass spectrometer (Waters). An Acclaim^{TM} 120 C18 column (130 × 3 mm, 3 μm particle size) was used. HPLC separation of products was achieved utilizing a binary gradient elution with acetonitrile with 0.05% of formic acid (component A) and water with 0.05% of formic acid (component B) controlled by the following program: 0 min. – 80% A; 20 min. – 100% A; 28 min. – 100% A. A flow rate of 0.5 mL/min was used. The samples were injected using a Rheodyne valve furnished with 5 μL sample loop.

During the HPLC analyses, full mass spectra were recorded in the range of m/z 200 - 800 with scan duration of 2 s. The electrospray ion source was operated in negative ion mode (ESI−), and thus $(M-1)^-$ ions, i.e. substituted phenolates were produced, mass-analyzed and detected. The ESI− settings were as follows: capillary voltage −2.7 kV, cone voltage 50 V, source temperature 100°C, desolvation temperature 200°C, desolvation gas (N_2) flow 300 L/h. For quantitative HPLC analysis, the standard addition method was used in connection with UV detector set at 280 nm. A mixture of c*is*- and *trans*-1,16-bis(3-hydroxyphenyl)hexadecene was used as an internal standard (for preparation and characterization of these compounds see chapter "Preparation and characterization of product **10**" in Supplementary material).

Cardanol conversions were determined from GC (using an internal standard). Conversion (*C*) was calculated according to Eq. 1 and yield (Y_i) of product *i* according to Eq.2.

$$C(\%) = 100(1- c_{card} / c^0_{card}) \qquad (1)$$

$$Y_i\ (\%) = 100(c_i / c^0_{card}) \qquad (2)$$

The experimental error in determination of cardanol conversion was ±2% (absolute) for all metathesis and cross-metathesis reactions.

Preparative thin-layer chromatography (TLC) was performed on Aldrich PLC Silica Gel 60 F_{254} 1 mm preparative plates using a mixture of hexanes : dichloromethane : diethylether / 6 : 3 : 1 as a mobile phase.

NMR spectra were recorded on a Varian ^{UNITY}*INOVA* 400 instrument (proton frequency 400 MHz) or Varian 300 NMR System in CD_2Cl_2 or $CDCl_3$. Chemical shifts (δ scale, ppm) were obtained by first order analysis. Spectra were referenced to the solvent signal δ (CD_2Cl_2) = 5.32 ppm, δ ($CDCl_3$) = 7.25 ppm for ^{1}H NMR and solvent signal δ(CD_2Cl_2) = 54.00 ppm, δ ($CDCl_3$) = 77.00 ppm for ^{13}C NMR.

The Ru content in catalysts and Ru leaching into the reaction mixtures were determined by ICP-MS at the Institute of Analytical Chemistry, Institute of Chemical Technology, Prague. Solid samples containing silica were decomposed in a microwave decomposition unit with the mixture of HF and HNO_3. For details see ref. [17].

3. Results and discussion

3.1. Metathesis of cardanol in batch reactor

HPLC-MS analysis revealed that in cardanol obtained from the supplier and used in all following experiments cardanol components (see Fig.1) were present in the molar ratio 3-(pentadeca-8,11,14-trienyl)phenol (**2**) : 3-(pentadeca-8,11-dienyl)phenol (**3**) : 3-(pentadec-8-enyl)phenol (**4**) : 3-(pentadecyl)phenol = 42.8 : 18.2 : 36.4 : 2.6. In addition to this the cardanol sample contained a certain amount of cardols impurities (8.6%). With regard to the practical applications we worked with cardanol as obtained without any purification. Moreover, the cardol impurities and their metathesis products were not taken into accounts.

Fig.3 shows conversion curves for cardanol metathesis over **1**/SBA-15 (0.09), and **1**/SBA-15 (1.0) (50 mg and 5 mg, respectively) at cardanol/Ru molar ratio 1000. Rapid onset of the reaction and high conversions are visible in both cases. The conversions achieved with **1**/SBA-15 (0.09) and **1**/SBA-15 (1.0) are practically the same. It is to expect because of the same substrate and Ru concentrations in the reaction mixture. The difference in the weight amounts of catalysts used and different concentrations of Ru centers on the catalyst surface have no visible effect under conditions applied.

The experiments with the same weight amounts (10 mg) of catalysts **1**/SBA-15 (0.09), **1**/SBA-15 (0.5), and **1**/SBA-15 (1.0), and 0.5 mmol of cardanol in the same solvent volume (Fig. S3 in Supplementary material) showed only slightly lower conversions for **1**/SBA-15 (0.5) in comparison with **1**/SBA-15 (1.0) at the early stages in accord with the lower Ru concentration in the system. The conversions after prolonged reaction time were the same. On the other hand very low conversions were achieved with **1**/SBA-15 (0.09) indicating very rapid deactivation of catalyst by impurities and/or by substrate in high excess. The cardanol/Ru ratio seems to be the main factor influencing the results of cardanol metathesis (see below).

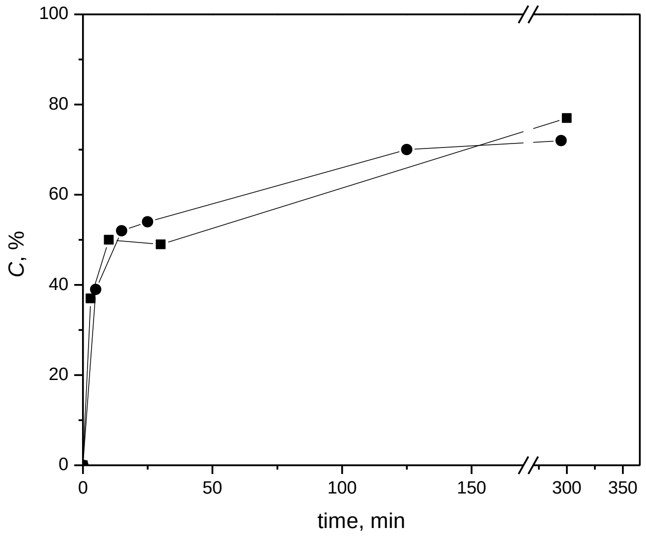


Fig. 3. Cardanol conversion vs. time for **1**/SBA-15 (0.09) - (●) and **1**/SBA-15 (1.0) - (■). Toluene, 35°C, cardanol/Ru = 1000, initial cardanol concentration c^0_{card} = 0.13 mol/L.

Fig. 4 shows the decrease in HPLC peak areas corresponding to individual cardanol components during metathesis reaction. Assuming the same extinction coefficient (UV detection at 208 nm) we can compare the consumption rates of individual components. The initial rate (i.e. the reduction of peak area in the first 3 min) decreased in the order **2** > **3** > **4**. After 300 min of the reaction, the components **2** and **3** were consumed nearly completely, however, about 40% of the original amount of component **4** persisted in the reaction mixture. This difference in consumption rates cannot be explained by different initial concentrations of cardanol components (initial concentrations of **2** and **4** do not differ too much, initial concentration of **4** is higher than that of **3**) but it reflects the participation of individual components in different metathesis reactions (see below).

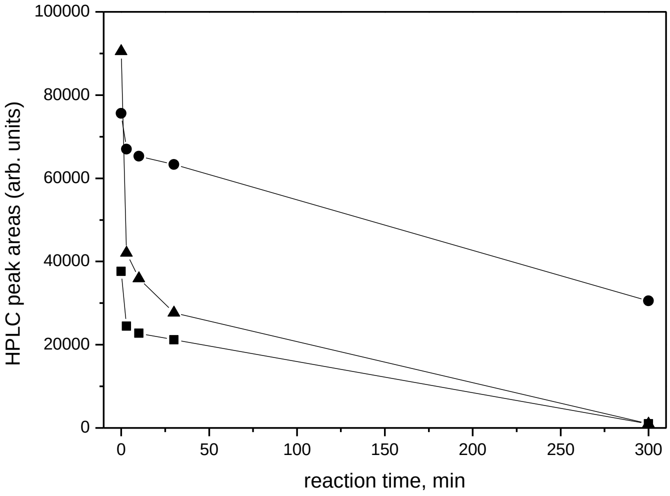


Fig. 4. Changes of HPLC peak areas of cardanol components **2** (▲), **3** (■), **4** (●) during metathesis reaction. **1**/SBA-15 (1.0), toluene, 35°C, cardanol/Ru molar ratio = 1000, c^0_{card}= 0.13 mol/L.

Theoretically, individual cardanol components can react in many self-metathesis and cross-metathesis reactions, giving rise numerous different alkenes and phenolic compounds. However, only some of them were found in considerable amounts. The reaction products contained (see a typical HPLC chromatogram in Fig.S4 and GC chromatogram in Fig.S5 in Supplementary material): 1,4-cyclohexadiene (**5**), 4-undecene (**6**), 7-tetradecene (**7**), 3-(non-8-enyl)phenol (**8**), 3-(dodec-8-enyl)phenol (**9**), and 1,16-bis(3-hydroxyphenyl)hexadecene (**10**). The yields of selected products (calculated from GC chromatograms) in the course of metathesis reaction over **1**/SBA-15 (0.09) and **1**/SBA-15 (1.0) are displayed in Fig.5. For **1**/SBA-15 (0.5) a similar product development was observed (Fig.S6 in Supplementary material). The common features of these developments are (i) rapid formation of **5** in yields corresponding to the consumption of **2**; (ii) rapid formation of **8,** however in considerably lower yields than the yields of **5** , (iii) formation of **9** (yield about 7%), (iv) very low yields of alkenes **6** and **7** even at high cardanol conversion (3%, 2%, respectively). The low yield of **7** is rather surprising, because the yield of **10** (calculated from HPLC-MS), was about 15%. Assuming **10** to be a product of self-metathesis of **4** [5]**,** **7** and **10** should be formed in approximately same amounts.

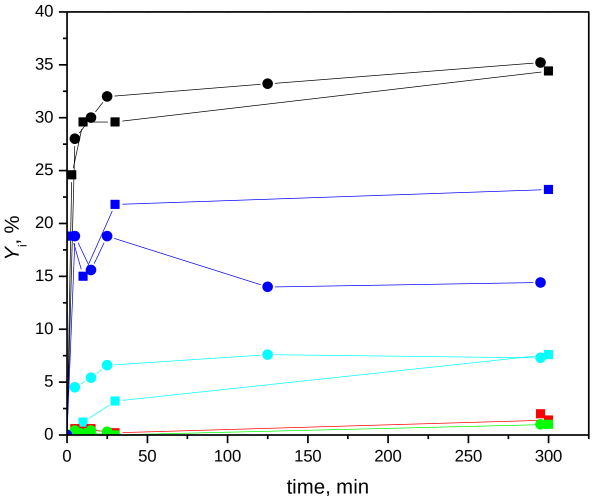
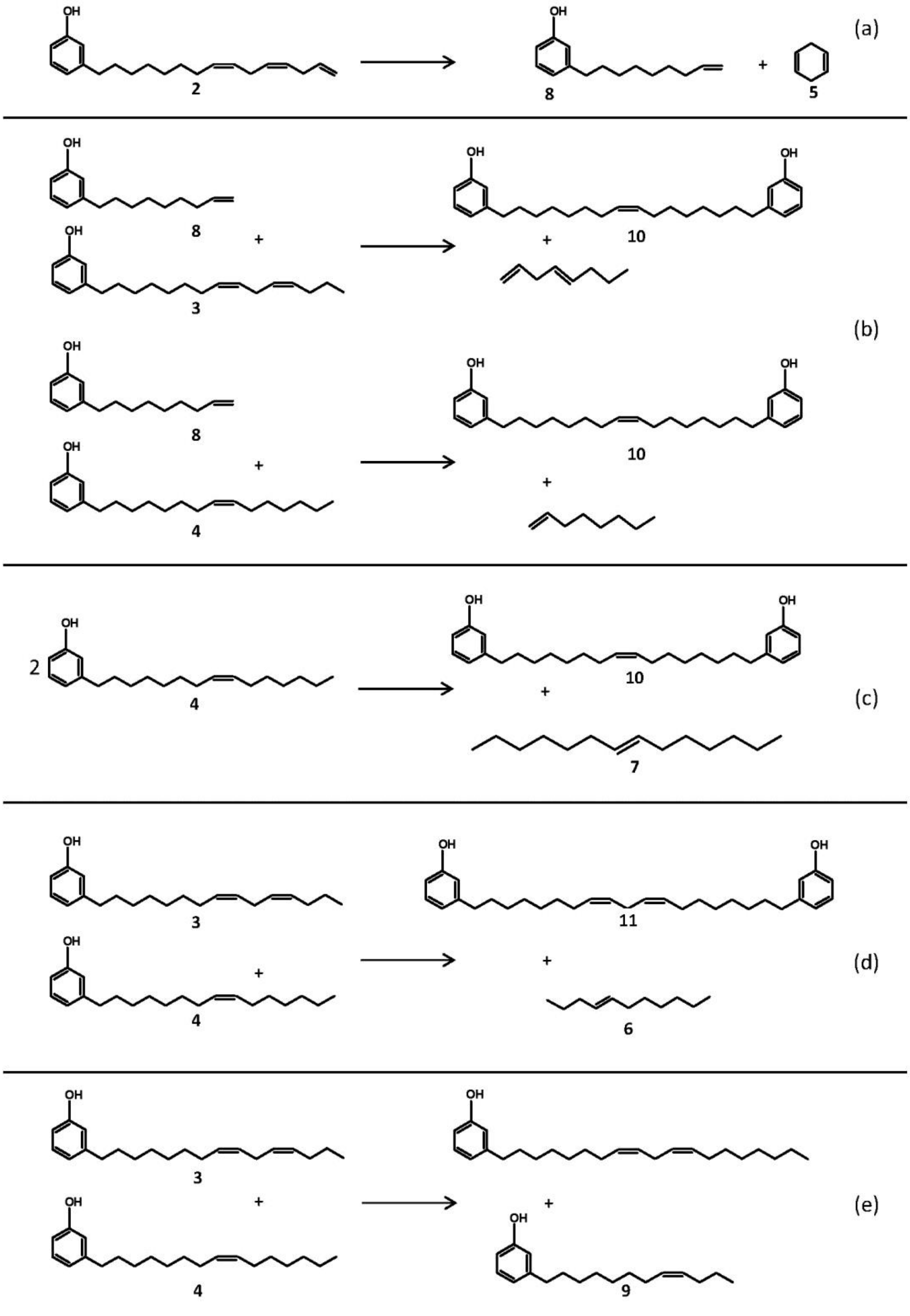


Fig. 5. Time development of selected products during cardanol metathesis over **1**/SBA-15 (0.09) - (●) and **1**/SBA-15 (1.0) - (■). Toluene, 35°C, cardanol/Ru = 1000, initial cardanol

concentration c^0_{card} = 0.13 mol/L. Products: **5** (black), **6** (green), **7** (red), **8** (blue), **9** (magenta).

To explain the product formation in a real cardanol mixture under conditions applied we set up a tentative scheme of the main reactions proceeding in this system (Scheme 1). A rapid consumption of **2** and formation of **5** in the short reaction times indicates the monomolecular self-metathesis of **2** (reaction (a) in Scheme 1). The second product of this self-metathesis reaction **8** was partially consumed in a consecutive reaction. As bisphenol compound **10** was found in a considerable amount even at the early stages of the reaction (when **7** was not observed), we suggest **8** reacted with **4** and **3** in cross-metathesis reactions (b) in Scheme 1. Hydrocarbons C_8H_{16} and C_8H_{14} were found in GC-MS, however, their quantification was not possible. Bimolecular self-metathesis of **4** - reaction (c) in Scheme 1 - seems to be strongly limited (maybe for steric reasons in coordination to the catalyst): corresponding tetradecene **7** was formed in very low amounts. Similarly, undecene **6** was formed in a low yield in cross-metathesis reaction (d) in Scheme 1. Product **9** - 3-(dodec-8-enyl)phenol - was formed in cross-metathesis of **3** and **4** - reaction (e) of Scheme 1.

It may be noticed, that the position of double bond in compounds in Scheme 1 is assumed in accord with metathesis mechanism. The double bond shift isomerization during metathesis in some extent cannot be excluded. *Cis-trans* isomerization during metathesis reaction was observed: starting cardanol is practically all *cis-*, during reaction *trans*-isomers were identified among cardanol components as well as among the reaction products.



Scheme 1. The formation of the main metathesis products in cardanol system.

To asses the possibility of higher TONs achievements, the reaction was performed using different substrate/Ru molar ratios (Fig.6). With increasing cardanol/Ru ratio TON increased till cardanol/Ru ratio 2500, when conversion 64% and the highest TON = 1600 were achieved. Further increase in the cardanol/Ru ratio led to the decrease in both final conversion and TON. Catalyst deactivation either by reaction with cardanol impurities or with cardanol itself occurred. In accord with the proposed reaction mechanism (Scheme 1) the yield of product **8** increased with increasing cardanol/Ru ratio up to cardanol/Ru = 2500 from 13% to 20% and the yield of **5** was kept on 39% (practically maximum possible yield). TON = 1600 is several times higher than that achieved in cardanol metathesis over Ru catalysts previously [13].

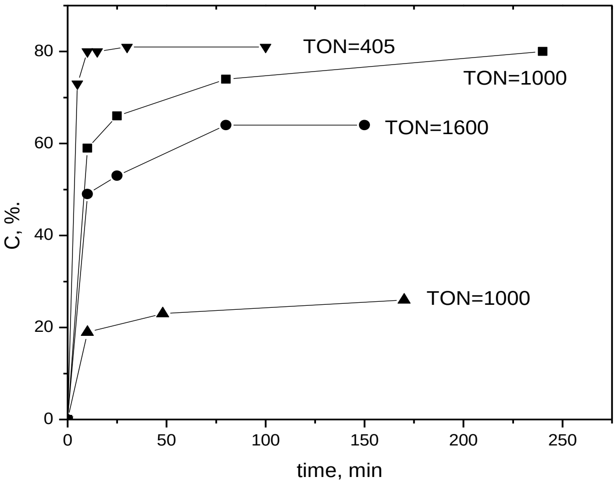


Fig. 6. Cardanol conversion curves at cardanol/Ru molar ratios = 500 (▼), 1250 (■), 2500 (●) and 4000 (▲). **1**/SBA-15 (0.09), toluene 1.2 mL, 35°C, c^0_{card} = 0.21mol/L.

3.2.Metathesis of cardanol in continuous flow reactor

Temperature 60 °C and cardanol concentration in the feed c^0_{card} = 0.15 mol/L were chosen as the optimal reaction conditions for cardanol metathesis in a flow system. For **1**/SBA-15 (0.09) it was found (see Table 2, No 4,5 and Fig. S7 in Supplementary material) that 50°C led to low initial conversion, on the other hand the temperature increase to 75°C caused very fast catalyst deactivation similarly as the doubled cardanol concentration in the feed. The effect of Ru content in catalyst is presented in Fig. 7 and Table 2, No 1-3. Cardanol conversion vs. time plots for **1**/SBA-15 (0.09), **1**/SBA-15 (0.5), and **1**/SBA-15 (1.0) clearly show that the catalyst stability is limited: after a certain period the cardanol conversion fell down. This period increased with Ru content in catalyst in the order **1**/SBA-15 (0.09) < **1**/SBA-15 (0.5) < **1**/SBA-15 (1.0). The average cardanol conversion (calculated from the cardanol conversion vs. time curve as cumulative amount of cardanol consumed in the experiment and the total amount of cardanol entered the reactor) increased in the same order, cumulative TON (calculated as the cumulative amount of cardanol consumed in the experiment divided by the amount of Ru in catalyst in the cartridge – both quantities in mol) in reverse order. **1**/SBA-15 (1.0) delivered the highest average cardanol conversion (59%), **1**/SBA-15(0.09) the highest cumulative TON (2500 and/or 2800). These TONs are higher than the highest TON achieved in batch reactor (1600).

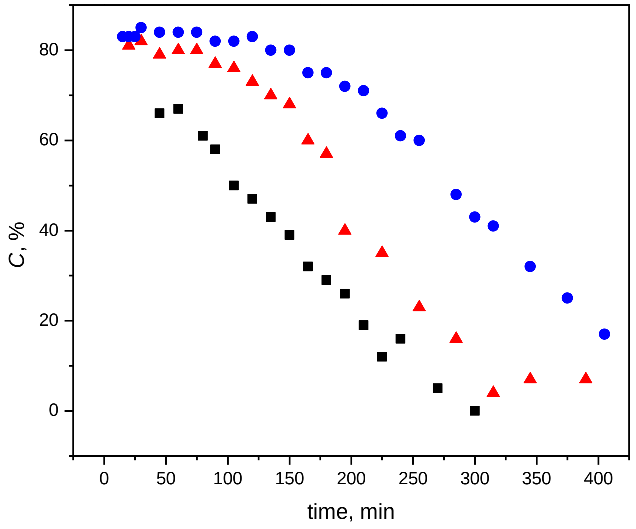


Fig. 7. Cardanol conversion vs. time for **1**/SBA-15 (0.09) (■), **1**/SBA-15 (0.5) (▲), and **1**/SBA-15 (1.0) (●). Flow reactor, toluene, 0.1mL/min, 60°C, c^0_{card} = 0.15 mol/L.

Table 2. Average cardanol conversions, cumulative TONs, and Ru leaching in flow system.

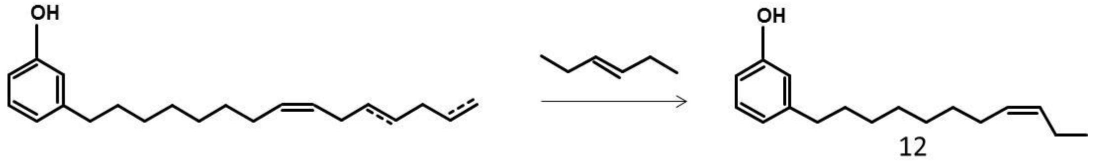
No	catalyst	T , °C	c^0_{card} , mol/L	Average conversion, C_A, %	Cumulative TON	Ru leaching [a, b]
1	**1**/SBA-15 (0.09)	60	0.15	30	2500	1.3%, 0.2 ppm
2	**1**/SBA-15 (0.5)	60	0.15	41	960	1.0%, 1.3 ppm
3	**1**/SBA-15 (1.0)	60	0.15	59	800	1.5%, 2.9 ppm
4	**1**/SBA-15 (0.09)	60	0.30	22	2800	–
5	**1**/SBA-15 (0.09)	75	0.15	31	200	7.0%, 1.7 ppm

Toluene, 0.1 mL/min, $C_A=100\int(c_{card}-c^0_{card}).dt/c^0_{card}.t$ (t = experiment time), [a] in % of original Ru content in catalyst, [b] in ppm related to the original cardanol amount.

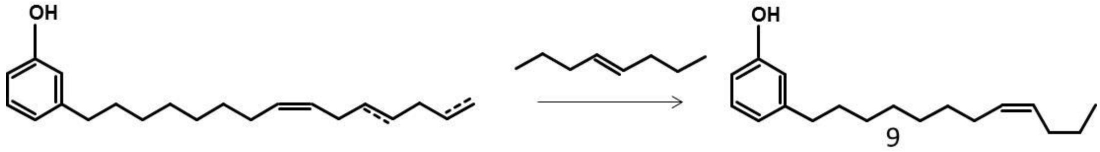
Catalyst leaching of **1**/SBA-15 (0.09), **1**/SBA-15 (0.5), and **1**/SBA-15 (1.0) in these experiments (determined from the collected liquid phase) increased with the increasing amounts of Ru in the catalysts from 0.2 ppm to 2.9 ppm with respect to the starting amount of cardanol (Table 2). Corresponding losses of Ru in catalysts were from 1.0 to 1.5% at 60°C and 7% at 75°C. Therefore, the reduction of Ru content in catalysts cannot be responsible for the continuous loss of their activity. On the other hand, the negligible concentration of Ru in a liquid phase ensured the acceptable level of product contamination by catalyst residues.

3.3. Cardanol cross-metathesis

Cross-metathesis of cardanol with linear alkenes and with unsaturated esters were studied both in batch and flow reactors. The results achieved in batch reactor are collected in Table 3. Cross-metathesis with symmetrical alkenes can be used for changing the lengths of aliphatic chain in cardanol molecule [10]. Using these reactions, phenol with 11 carbon atom chain (product **12,** eq. 3) can be prepared from cardanol and 3-hexene, and similarly phenol with 12 carbon atom chain (product **9**, eq. 4) from cardanol and 4-octene. Product **9** may arise also from cardanol metathesis according Scheme 1(e) (see above). If alkene is used in excess, phenols **9** and **12** are produced in high yields (see Table 3). On the other hand, complementary hydrocarbons C_{10} and C_{11} (see Scheme S1 and S2 and Figs S8 and S9 in Supplementary material) are formed in significantly lower amounts than **9** and **12**. Negligible amounts of phenol **8** indicates its possible reactions with 3-hexene and 4-octene under formation of **9** and **12**.

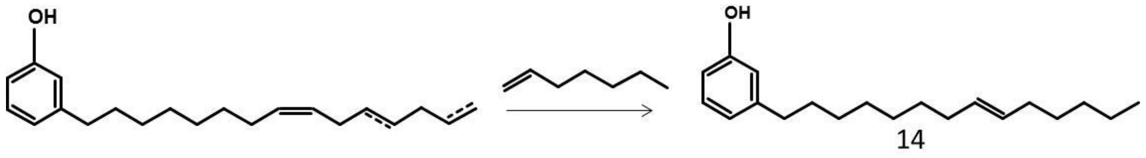


(3)



(4)

1-hexene and 1-heptene gave rise to phenols with aliphatic chains having 13 and 14 carbon atoms, respectively (eqs 5 and 6). However, their yields were only 25 and 27%, respectively, which is connected with a consumption of considerable amounts of both 1-alkene in self-metathesis reactions leading to 5-decene and 6-dodecene, respectively (see Schemes S3 and S4 and Figs S10 and S11 in Supplementary material). There is an additional difference in behavior of 1-akenes in cross-metathesis with cardanol: product **8** was found in high amounts (yields of 46 and 52%, respectively). These amounts are higher than that of **2** in original cardanol, which suggests that **8** must be formed also in a reaction of 1-alkenes with **3** or **4**. Thus cross-metathesis with 1-alkenes may represent an alternative way to product **8** in addition to cardanol ethenolysis [9,13].



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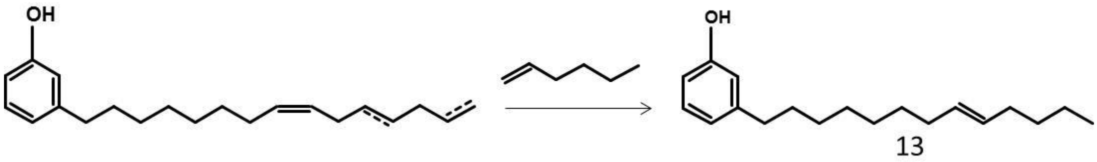
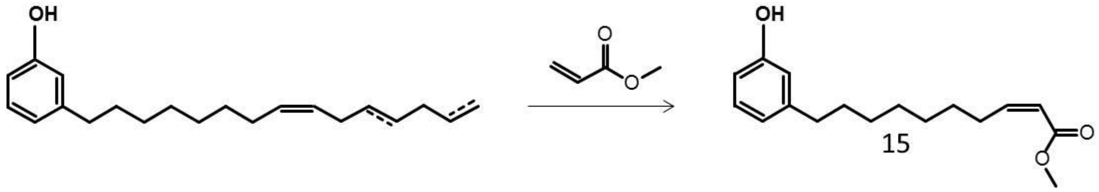
(6)



Despite its electron-deficient double bond methyl acrylate reacted smoothly under mild reaction conditions and delivered expected phenol derivative **15** (eq.7) in 45% yield (see Table 3, No 5). Long chain ester **16** was formed in a significantly lower amount as well as product **8** (see Scheme S5 and Fig.S12 in Supplementary material). Product **15** was isolated by TLC and characterized by NMR and MS (see Fig.S13, Supplementary material). Changing **1**/SBA-15 (0.09) for **1**/SBA-15 (0.5) (Table 3, No 6) higher cardanol conversion and higher yield of product **15** were achieved in a shorter reaction time (1h) as expected. TON however decreased more than 4 times.

Cis-1,4-diacetoxybut-2-ene (DAB) contains two ester groups in the molecule. It might be the reason for a rapid catalyst deactivation and rather low yield of product **17** under conditions applied (eq. 8, Table 3, No 7). **A**liphatic acetate **18** was formed even in a lower amout (see Scheme S6 and Fig. S14 in Supplementary material). Product **17** was isolated and characterized similarly as product **15** (see Fig.S15**,** Supplementary material).



(7)

(8)

Table 3. Cardanol cross-metathesis in batch reactor

	Co-substrate	Reaction time, h	Cardanol conversion, *C*, %	Selected products	Yield of selected products, Y_i, %
1	3-hexene	5	93	**12** **8**	$Y_{12} = 68$ $Y_8 = 1$
2	4-octene	5	72	**9** **8**	$Y_9 = 43$ $Y_8 = 3$
3	1-hexene	5	94	**13** **8**	$Y_{13} = 25$ $Y_8 = 46$
4	1-heptene	3.5	90	**14** **8**	$Y_{14} = 27$ $Y_8 = 52$
5	methyl acrylate	5	86	**15** **8**	$Y_{15} = 45$ $Y_8 = 5$
6	methyl acrylate*	1	95	**15** **8**	$Y_{15} = 69$ $Y_8 = 5$
7	*cis*-1,4-diacetoxybut-2-ene	5	42	**17** **8**	$Y_{17} = 8$ $Y_8 = 14$

1/SBA-15 (0.09), toluene, 35°C, co-substrate/cardanol/Ru molar ratio = 2000/500/1, c^0_{card} = 0.21 mol/L. * 1/SBA-15 (0.5) , co-substrate/cardanol/Ru molar ratio = 400/100/1.

Cross-metathesis of cardanol with selected co-substrates was also carried out in a flow system. **1**/SBA-15 (0.5) and temperature 60°C were used. **1**/SBA-15 (0.5) was chosen because fast catalyst deactivation was observed for **1**/SBA-15 (0.09) in some cases. For example in the system cardanol + 3-hexene (molar ratio1:4) cardanol conversion only 11% was achieved. Table 4 summarizes the main results. Average cardanol conversion and cumulative TON were calculated as in the previous section. From the conversion vs. time plot (Fig. S16 in Supplementary material) it is seen that cross-metathesis with symmetrical alkenes proceeded in a similar way as metathesis of cardanol. Especially for 3-hexene, high TON (1550) and high yield of product **12 (**49%) were achieved.

For methyl acrylate and DAB, however, the catalyst deactivation was faster than for cross-metathesis with alkenes and therefore the TONs and yields fell down. For cross-metathesis with methyl acrylate (Table 4, No 3) Ru leaching was established as 4.5% with respect to the Ru catalyst content and 4.9 ppm with respect to cardanol. This leaching is significantly higher than that found for cardanol metathesis under same conditions (Table 2), indicating a possible effect of substrate polarity on Ru leaching. Nevertheless, this leaching can be still considered as small, confirming strong bonding interaction between **1** and SBA-15 support.

Table 4. Cardanol cross-metathesis in flow system

No	co-substrate	Time, h	Average cardanol conversion, C_A, %	Cumulative TON	Cumulative yield of the key product, %
1	3-hexene	4.5	72	1550	$Y_{12} = 49$
2	4-octene	5.7	50	1250	$Y_9 = 29$
3	Methyl acrylate	4.25	47	905	$Y_{15} = 11$
4	*cis*-1,4-diacetoxybut-2-ene	5.7	28	540	$Y_{17} = 23$

1/SBA-15 (0.5), toluene, 60°C, c^0_{card} = 0.15 mol/L, co-substrate/cardanol molar ratio = 4, flow rate 0.1 mL/min, $C_A = 100 \int (c_{card} - c^0_{card}).dt / c^0_{card}.t$ (t = experiment time), cumulative TON with regard to cardanol.

4. Conclusions

Quaternary ammonium tagged Ru complex of Hoveyda-Grubbs type (AquaMet SIPr) immobilized on SBA-15 mesoporous molecular sieve by non-covalent interactions was proved as efficient catalyst for cardanol metathesis under mild conditions (35°C, toluene, 0.1 mol% of catalyst). Cardanol was used without any purification as a mixture of components. Metathesis reaction proceeded rapidly and high cardanol conversion (more than 80%) was achieved.

Time development of concentrations of individual cardanol components as well as of selected products during metathesis allowed us to set up a tentative scheme of reactions proceeding in this complex system under applied reaction conditions. Triply unsaturated cardanol component reacted very rapidly by self-metathesis under formation of 1,4-cyclohexadiene and 3-(non-8-enyl)phenol. Then 3-(non-8-enyl)phenol reacted by cross-metathesis with di- and mono-unsaturated cardanol components under formation of biphenolic compounds.

The catalyst was successfully tested in a flow system (60°C, toluene, 0.1 mL/min). The cumulative TON achieved was 2500, which surpassed the maximum TON in batch reactor (1600). The Ru leaching was low: from 1.0 to 1.5% of the original Ru content in catalyst, which corresponded to the possible product contamination with Ru in the range 0.2 – 2.9 ppm. However, catalyst stability was limited: after certain period cardanol conversion fell down. Catalyst deactivation probably by impurities or reaction with substrate itself occurred.

The catalyst was tested also in cross-metathesis of cardanol with alkenes (1-hexene, 1-heptene, 3-hexene, 4-octene) and unsaturated esters (methyl acrylate, 1,4-diacetoxybutene-2). The cross-metathesis with alkenes effectively changed the length of cardanol aliphatic chain. The cross-metathesis with esters allowed the introduction of ester group on the end of cardanol aliphatic chain. Especially in the case of cross-metathesis with methyl acrylate, high cardanol conversion and high yield of cross-metathesis product were achieved.

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Appendix: Supplementary material.

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