



Ultrasonic-assisted ruthenium-catalyzed one-pot synthesis of biscoumarins

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ABSTRACT

The Ru-grafted zeolite beta was found to be an excellent heterogeneous catalyst for one-pot synthesis of biscoumarins. This reaction was carried out under reflux condition and ultrasonic irradiation. On the other hand, the catalyst could be recovered for the subsequent reactions and reused without appreciable loss of activity.

Indexing terms/Keywords

Ultrasonic irradiation; heterogeneous catalysis; ruthenium; zeolite beta; schiff-base condensation; biscoumarin.



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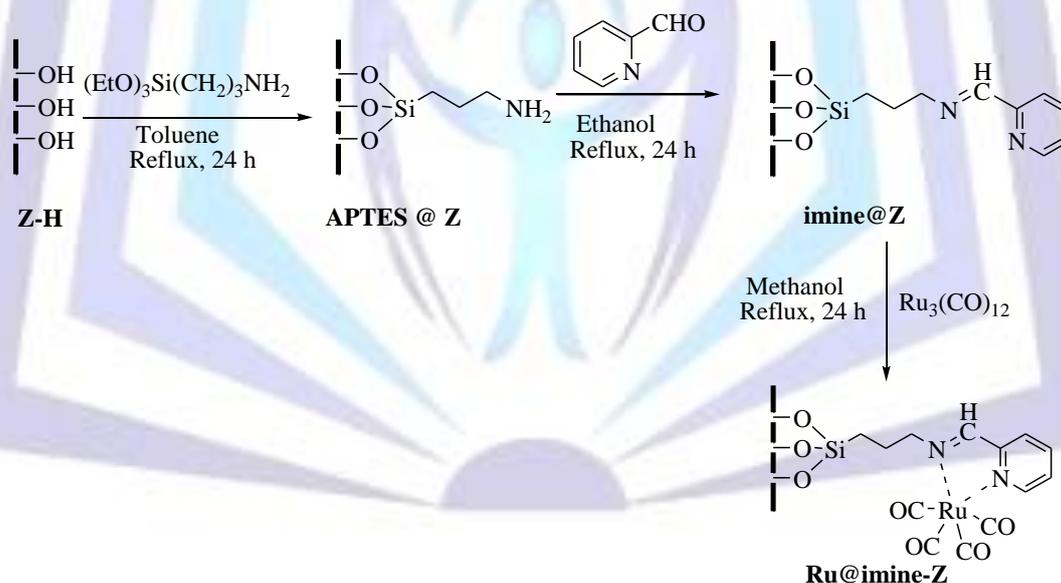
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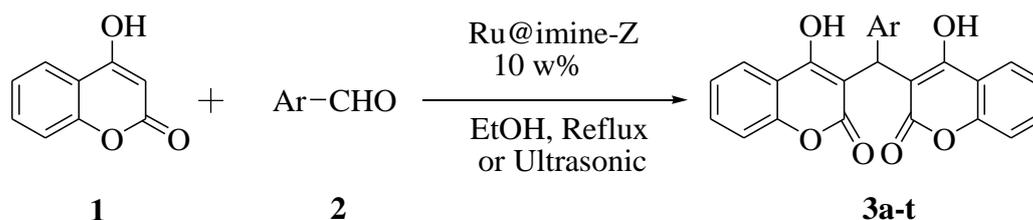
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1. INTRODUCTION

Ruthenium complexes have been known as versatile and useful catalysts for many organic transformations [1, 2]. Although, homogeneous ruthenium catalysts are often very much active and selective producing excellent yields, but difficult separation from the reaction media limits their application [3]. On the other hand immobilization of homogeneous catalysts onto inorganic matrices combines the advantages of homogeneous and heterogeneous catalysis [4]. Ruthenium species supported on a variety of supports such as montmorillonite K10, polystyrene, Al_2O_3 , Silica, Micelle templated silica (MTS), MCM-41 and FAU-Y zeolite have been reported in literature [5-13]. Meanwhile zeolite beta with superior physicochemical properties such as large pore size, high silicon to aluminum ratio, high acid strength and thermal stability could be a good framework for the immobilization of a variety of catalytic species. Developing ways to synthesize coumarins has been of considerable interest due to their wide range of biological and therapeutic properties such as anticoagulant, insecticidal, antihelminthic, hypnotic, antifungal, and HIV protease inhibition activities [14-16]. Furthermore, these heterocyclic compounds can be employed as additives to food, cosmetic [17] and optical brightening agents [18]. A number of coumarins are also available from natural sources [19-21]. Biscoumarins, the bridge substituted dimers of 4-hydroxycoumarin, have diverse biological activities such as anticoagulant [22], antioxidant [23], anticancer [24], cytotoxicity [25], and urease inhibition [26]. Moreover, cytotoxic activity of lanthanum (III) complexes of biscoumarins is reported [27]. Condensation reaction between 4-hydroxycoumarin and various aldehydes in the presence of catalyst is a straightforward approach for the synthesis of biscoumarins. A variety of reagents such as molecular iodine [28], tetrabutylammonium bromide (TBAB) [29], MnCl_2 [30], sodium dodecyl sulfate (SDS) [31], SO_3H functionalized, ionic liquids [32], $\text{Zn}(\text{Proline})_2$ [33], 3-methyl-1-(4-sulfonic acid)butylimidazolium hydrogensulfate $[\text{MIM}(\text{CH}_2)_4\text{SO}_3\text{H}][\text{HSO}_4]$ [34], Sulfated titania [35], SiO_2Cl [36] and Poly(4-vinylpyridinium) perchlorate $[\text{P}(4\text{-VPH})\text{ClO}_4]$ [37] have been employed to accomplish this transformation. Furthermore, microwave irradiation has been utilized for this synthesis [38, 39]. In spite of the merits of aforementioned routes, some of them suffer from the severe drawbacks, such as long reaction times, tedious work-up procedure and use of expensive and toxic catalysts. Therefore, development of an efficient catalytic system for the synthesis of biscoumarins would be highly desirable. In our previous work, we have reported an efficient method for the synthesis of biscoumarin derivatives using $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ as a homogeneous catalyst [40]. In an attempt to heterogenize homogeneous ruthenium compounds, recently we have explored an efficient protocol for the synthesis of a new ruthenium bound heterogeneous catalyst through Schiff-base condensation reaction between 3-aminopropyltriethoxysilane (APTES) functionalized zeolite beta and 2-pyridine carbaldehyde followed by complexation with $\text{Ru}(\text{CO})_4$ (Ru@imine-Z) (Scheme 1) [41]. In this study, this functionalized microporous material was used as an effective heterogeneous catalyst for the synthesis of biscoumarins (3a-t) (Scheme 2).



Scheme 1: Immobilization of ruthenium onto imine-functionalized zeolite beta through coordinative attachment



Scheme 2: Synthesis of biscoumarins in the presence of Ru@imine-Z



2. EXPERIMENTAL

2.1. Chemicals and apparatus

All the commercial organic reagents and solvents were purchased from Merck and used without further purification. Tetraethylammonium hydroxide (TEAOH, 20%), sodium chloride (99.5%), potassium chloride (99.5%) and sodium hydroxide (98%) were obtained from Merck. Sodium aluminate (56 w% Al₂O₃, 37 w% Na₂O) as alumina source purchased from Technical company. Ru₃(CO)₁₂ (99 %) was purchased from Acros. Degussa aerosil as silica source was used for the synthesis of zeolite beta. Deionized water was used in the present study. XRD patterns were recorded on a Philips PW1840 diffractometer with Cu-K α radiation (1.5418 Å), and scan rate 0.1° 2 θ /s and within a range of 2 θ of 4°–70°. Scanning electron micrographs were taken on a LEO 1430 VP instrument. The amount of ruthenium content was measured by inductively coupled plasma (ICP; Labtam 8440 plasma lab). The specific surface area based on nitrogen physisorption was determined by Sibata surface area apparatus 1100. Ultrasound device Astra 3D (9.5 L, 45 kHz frequency, input power with heating, 305 W, number of transducers, 2) from TECNO-GAZ was used. IR spectra were recorded on a Perkin-Elmer model spectrum one using KBr plates in the range of 400–4000 cm⁻¹. ¹H and ¹³C NMR spectra were recorded on Bruker Advance spectrometer at 400 and 100 MHz, respectively in CDCl₃ or DMSO-d₆ using TMS as an internal standard. Melting points were measured on a BÜCHI Melting point B-540 apparatus and are uncorrected. Elemental analysis (CHN) was performed on Carlo-Erba EA1110 CNNO-S instrument.

2.2. Catalyst Preparation

Immobilization of Ru₃(CO)₁₂ onto imine-functionalized zeolite H-beta was described in our recent work [41].

2.3. General procedure for the synthesis of biscoumarin derivatives under thermal conditions

To a mixture of 4- hydroxycoumarin (2 mmol) and aldehyde (1 mmol), catalyst (10 w% based on all substrates) was added. The mixture was stirred for appropriate time in ethanol (5 mL) under reflux condition. After completion of the reaction (as evidenced by TLC) and evaporation of ethanol, Ethyl acetate (20 mL) was added and the mixture was centrifuged to separate the catalyst. The filtrate was concentrated and the crude solid product was recrystallized from ethanol to afford pure product. The recycled catalyst was washed with ethyl acetate and acetone. After being dried it can be reused without further purification. All of the products were known and identified by comparison of their melting points and spectral data with those reported in the literature.

2.4. Typical procedure for the synthesis of biscoumarins under sonochemical conditions

To a mixture of 4- hydroxycoumarin (2 mmol), aldehyde (1 mmol), and ethanol (2 mL) was added catalyst (10 w% based on all substrates) and the reaction mixture was exposed to ultrasonic irradiation at room temperature for appropriate time, as shown in Table 2, entries 1-20. The progress of the reaction was followed by TLC. After completion of the reaction and evaporation of ethanol, Ethyl acetate (20 mL) was added and the mixture was centrifuged to separate the catalyst. The filtrate was concentrated and the crude solid product was recrystallized from ethanol to afford pure product.

3. RESULTS AND DISCUSSION

In order to study the optimization of reaction conditions, the synthesis of compound 3b was chosen as a model reaction (Scheme 2, Table 1). Firstly, we examined the reaction using ethanol as a solvent. In a simple experimental procedure, to a mixture of 4-nitrobenzaldehyde (1 mmol) and 4-hydroxycoumarin (2 mmol) in ethanol (5 mL), Ru@imine-z (5 w%, 24 mg) was added and the resulting mixture was stirred under reflux condition for 25 minute, to give, after workup, a 80% yield of compound 3b (Table 1, entry 1). To find out the optimum quantity of catalyst, the reaction was carried out under reflux conditions using different quantities of catalyst (Table 1, entries 2-4). It was found that the best results were obtained in the presence of 10 w% of Ru@imine-Z (Table 1, entry 2). Larger amount of catalyst, however, had no significant effect on the yield. Conducting the same reaction, by using 20 w% (95 mg) of activated zeolite (Z-H), led to low yield of the desired product (25%) after 2 h (Table 1, entry 5). The effect of temperature was also studied by carrying out the model reaction in the presence of 10 w% of Ru@imine-Z at room temperature, which gave a 50 % yield of the desired product after 24 hr (Table 1, entry 6). To investigate the effect of solvent, the model reaction was accomplished in various solvents, such as ethanol, methanol, acetonitrile, tetrahydrofuran and dichloromethane at different reflux temperatures (Table 1, entries 7-10). As shown in Table 1, ethanol was chosen as the best solvent. Finally, the model reaction was carried out under homogeneous catalytic system which gave the corresponding products in high yields (Table 1, entries 11-12).

Using these optimized reaction conditions, the scope and efficiency of the reaction were explored for the synthesis of a wide variety of substituted biscoumarins. A series of aromatic and heterocyclic aldehydes were selected to undergo the condensation in the presence of Ru@imine-z. As shown in Table 2, aromatic aldehydes carrying either electron-donating or electron-withdrawing substituents reacted efficiently giving excellent yields (85-95%) (Table 2, entries 2-17). It is also noteworthy that the electronic properties of the aromatic ring have an effect on the reaction time. The aromatic aldehydes bearing electron-withdrawing groups reacted somehow, faster than those bearing electron-releasing groups. Furthermore, heterocyclic aldehydes could react smoothly to give the corresponding products in good yields (85–92%) (Table 2, entries 18–20). To improve efficiency, we carried out this reaction under ultrasonic irradiation. As it is shown in Table 2, this method affords the desired products in excellent yields in rather short times.

Table 1. Screening of the reaction conditions for the synthesis 3,3'-(4 nitrophenylmethylene)bis-(4-hydroxy-2H-chromen-2-one) (3b).

Entry	Solvent	Temp (°C)	Amount of catalyst (w%)	Time (min)	Yield (%)
1	EtOH	80	5	25	80
2	EtOH	80	10	25	95
3	EtOH	80	15	25	95
4	EtOH	80	20	25	95
5	EtOH	80	20	120	25 ^a
6	EtOH	r.t.	10	1440	50 ^b
7	MeOH	65	10	45	92
8	CH ₃ CN	80	10	60	90
9	THF	70	10	90	80
10	CH ₂ Cl ₂	40	10	120	30
11	EtOH	80	5	25	92 ^c
12	H ₂ O	80	5	25	90 ^d

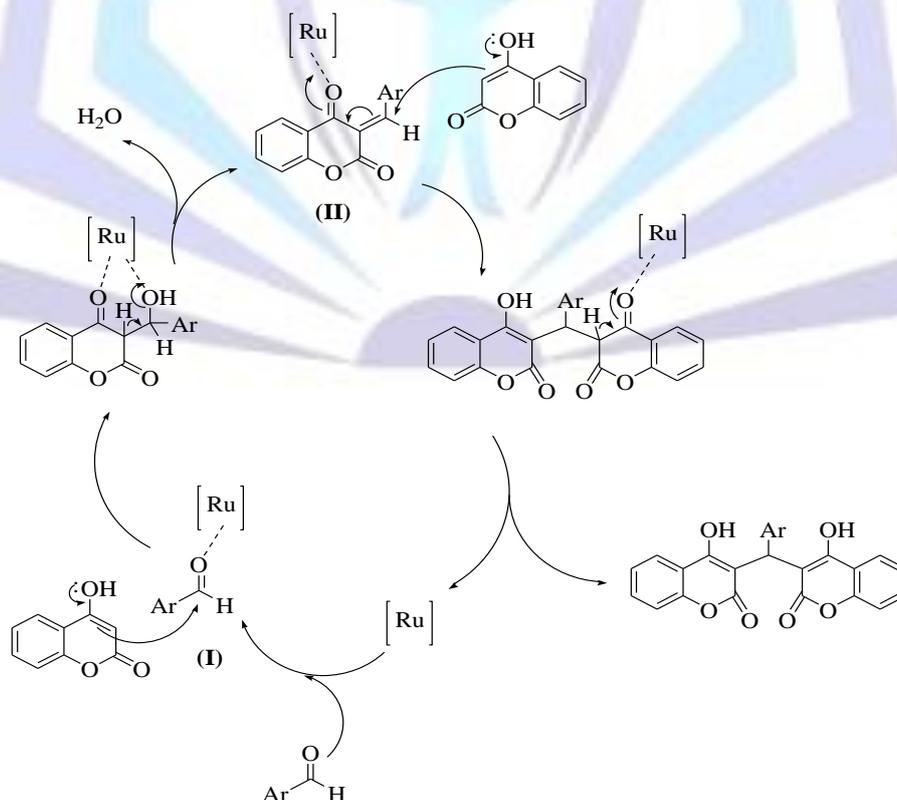
^a Activated zeolite was used as a catalyst.

^b Reaction was accomplished at room temperature.

^c Ru₃(CO)₁₂ (5 mol %) was used as a homogeneous catalyst.

^d RuCl₃.*n*H₂O (5 mol %) was used as a homogeneous catalyst.

According to the literatures [1-3], we think that heterogenized ruthenium catalyzes the reaction as a mild Lewis acid. The mechanism was tentatively proposed in scheme 3. As it is shown, prior activation of the carbonyl group of aldehyde by Ru to give intermediate I, followed by Knoevenagel condensation with 4-hydroxycoumarin provides unsaturated intermediate II. Michael addition of intermediate II with second molecule of 4-hydroxycoumarin and subsequent tautomeric proton shift affords the desired product (Scheme 3).


Scheme 3: Proposed mechanism for the synthesis of biscoumarins in the presence of Ru@imine-Z as catalyst

**Table 2. Synthesis of biscoumarins in the presence of Ru@imine-Z under reflux condition and ultrasonic irradiation.**

Entry	Ar	Product	Reflux Condition		Ultrasonic Irradiation		M.P. (°C)	
			Time (min)	Yield ^a (%)	Time (min)	Yield ^a (%)	Found	Reported [Ref.]
1	C ₆ H ₅	3a	30	90	5	92	213-215	215 [38]
2	4-NO ₂ C ₆ H ₄	3b	25	95	4	95	236-238	238-239 [39]
3	3-NO ₂ C ₆ H ₄	3c	25	88	5	92	212-214	212-215 [38]
4	2-NO ₂ C ₆ H ₄	3d	30	85	7	90	199-201	198-200 [34]
5	4-ClC ₆ H ₄	3e	20	92	4	95	260-262	261-263 [34]
6	3-ClC ₆ H ₄	3f	25	90	5	90	228-230	228-230 [31]
7	2-ClC ₆ H ₄	3g	25	88	5	90	202-204	201-203 [34]
8	4-FC ₆ H ₄	3h	20	90	4	97	214-216	213-215 [31]
9	3,4-F ₂ C ₆ H ₃	3i	30	92	5	95	261-263	262-264 [40]
10	3-C ₆ H ₅ OC ₆ H ₄	3j	30	90	6	92	219-221	218-220 [40]
11	4-OHC ₆ H ₄	3k	25	90	5	92	221-223	222-224 [28]
12	2-OHC ₆ H ₄	3l	30	85	6	88	252-254	254-256 [28]
13	4-CH ₃ C ₆ H ₄	3m	35	90	4	90	268-270	266-269 [34]
14	4-CH ₃ OC ₆ H ₄	3n	35	90	6	94	250-252	250-252 [34]
15	3,4-(CH ₃ O) ₂ C ₆ H ₃	3o	40	85	8	90	267-269	266.5-268 [22]
16	4-(CH ₃) ₂ NC ₆ H ₄	3p	30	94	7	94	223-225	222-224 [31]
17	4-CH ₃ SC ₆ H ₄	3q	20	88	8	90	259-260	258-260 [37]
18	5-Methyl-2-thiophenyl	3r	30	92	7	95	350	>300 [33]
19	3-Indolyl	3s	40	85	7	92	238-240	238-240 [40]
20	4-pyridyl	3t	25	90	5	90	252-254	252-254 [33]

Note: All products were characterized by ¹H NMR, ¹³C NMR and IR data.

^a Yields refer to isolated pure products.

To compare the efficiency of our catalyst with respect to the previously reported catalysts for the preparation of biscoumarins, the results for the synthesis of 3b as a model compound, employing these catalysts, are tabulated in Table 3. As it is shown, zeolite supported ruthenium (Ru@imine-Z) acts as effective catalyst with respect to reaction time and yield of the product.

Table 3. Comparison of our results with those reported in the literature for the Synthesis of 3,3'-(4-nitrophenylmethylene)bis-(4-hydroxy-2H-chromen-2-one) (3b).

Entry	Catalyst (amount)	Solvent	Temp (°C)	Time (min)	Yield (%)	Ref.
1	SiO ₂ Cl (75 mg)	CH ₂ Cl ₂	40	210	85	36
2	SDS (20 mol%)	H ₂ O	60	180	98	31
3	SO ₃ H-functionalized ionic liquids (10 mol%)	-	70	120	96	32
4	TiO ₂ /SO ₄ ²⁻ (10 w%)	H ₂ O	80	30	88	35
5	I ₂ (10 mol%)	H ₂ O	100	28	95	28
6	TBAB (10 mol%)	H ₂ O	100	25	91	29
7	RuCl ₃ .nH ₂ O (5 mol%)	H ₂ O	80	25	90	40
8	Ru@imine-z (10 w%)	EtOH	80	25	95	-



The reusability of the catalyst was investigated in the synthesis of 3,3'-(4-nitrophenylmethylene)bis-(4-hydroxy-2H-chromen-2-one) (3b). The catalyst was separated after each run, washed thoroughly with ethyl acetate and acetone, dried in an oven at 60 °C and reused in subsequent runs. The recovered catalyst was reused in subsequent reactions without significant decrease in activity even after five runs (Table 4). Moreover, ICP analysis showed 20 % decrease in the Ru content on the solid catalyst before and after five run use.

Table 4. Reusability of the catalyst for synthesis of compound 3b.

Run No.	Yield (%)
1	95
2	92
3	90
4	88
5	88

4. CONCLUSION

In brief, we have introduced a simple strategy to heterogenize a homogeneous ruthenium complex onto zeolite beta. The resulted catalyst was applied in the synthesis of biscoumarin derivatives and the corresponding products were obtained in excellent yields. Moreover, our heterogeneous catalyst could retain high activity of the homogeneous counterpart catalyst.

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Author' biography with Photo



Khalil Tabatabaeian was born in Mashhad, Iran. He received his B.Sc in Pure Chemistry from Mashhad University, Iran in 1976. He started his doctoral studies in Sheffield University, England, and obtained his Ph.D. degree in 1980. He has been a faculty member of Guilan University since 1982. His current research interest includes heterogenization of homogeneous catalysts, through covalent attachment to inorganic matrices such as zeolites and metal organic frameworks which combines the advantages of homogenous and heterogeneous catalysis.

