

루테늄 지르코니아 불균일 촉매를 이용한 알켄 또는 알킨의 효과적인 산화절단반응

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Efficient Oxidative Scission of Alkenes or Alkynes with Heterogeneous Ruthenium Zirconia Catalyst

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초 록

알켄 또는 알킨의 산화 반응이 루테늄 지르코니아 불균일 촉매에 의해 매우 선택적이며 효율적으로 전환되었다. 절단 반응을 통해, C-C 이중 결합은 알데히드 관능기로, 삼중 결합은 다이케톤 또는 카르복시산으로 전환되었는데, 다양한 기질들이 30 °C에서 $\text{PhI}(\text{OAc})_2$ 산화제와 dichloromethane 및 물(각각 5 mL와 0.5 mL)의 혼합 용매 조건에서 반응이 수행되었다. 사용된 촉매 $\text{Ru}(\text{OH})_x/\text{ZrO}_2$ 는 이 절단 반응에 대해 기존의 다른 루테늄 기반 불균일 또는 균일 촉매들보다 더 좋은 활성과 선택성을 보였다. 반응이 진행되는 동안, 제조된 촉매의 기계적인 물성은 안정적이었고, 급속의 침출은 전혀 보이지 않았다. 불포화된 탄화수소들의 산화적 절단에 대해, 합성된 촉매는 여러 번 재사용해도 그 촉매의 성능을 그대로 유지하였다.

Abstract

The efficiency of a heterogeneous ruthenium zirconia catalyst ($\text{Ru}(\text{OH})_x/\text{ZrO}_2$) was demonstrated to the selective oxidative transformation of alkenes or alkynes. The scissions of C-C double bonds to aldehydes and triple bonds to diketones or carboxylic acids were carried out with (diacetoxyiodo)benzene as an oxidant under dichloromethane (5 mL)/water (0.5 mL) solvent system at 30 °C for wide range of substrates. The $\text{Ru}(\text{OH})_x/\text{ZrO}_2$ composite showed higher catalytic activity and selectivity than other ruthenium-based homogeneous or heterogeneous catalysts for the scission reaction. The catalyst exhibited a high mechanical stability, and no leaching of the metal was observed during the reaction. These features ensured the reusability of the catalyst for several times for the oxidative cleavage of unsaturated hydrocarbons.

Keywords: heterogeneous, ruthenium zirconia catalyst, alkenes or alkynes, scission, reusability

1. Introduction

The incorporation of oxygen functional group into the existing molecular framework[1] has been put on a great interest synthetically since the large structured compounds can be degraded into useful products by the scission of C=C and C≡C bonds[2]. The catalytic cleavage

of unsaturated hydrocarbons is an imperative reaction in synthetic chemistry[3,4] as these reactions result in the formation of variety of products such as epoxides, carbonyl compounds, diols, etc. These carbonyl compounds are not only important as synthetic intermediates but also extensively used in fine chemicals, pharmaceuticals, and agriculture[5,6]. Various methodologies for the selective oxidative transformation of alkenes or alkynes to aldehydes and ketones has been reported so far by the early pioneers[7-12] but the process is still not easy because the output of the reaction is highly influenced by the reaction conditions[13]. Ozonolysis has been employed as the most commonly used method for oxidative transformation along with other techniques such as use of KMnO_4 [14], oxone[15,16], NaIO_4 [17], *m*-CPBA

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Table 1. Oxidative Cleavage Transformation of cis-1,2-diphenylethylene Using Various Catalysts^[a]

Entry	Catalyst	Temp. (°C)	Conv. (%)	Select. (%)
1	Ru(OH) _x /ZrO ₂	30 °C	> 99	93
2	Ru(OH) _x /ZrO ₂	R.T.	99	84
3	Ru(OH) _x /MgO	30 °C	> 99	57
4	RuCl ₃ · xH ₂ O	30 °C	> 99	75
6	[Ru(<i>p</i> -cymene)Cl ₂] ₂	30 °C	> 99	74
7	Ru ₃ (CO) ₁₂	30 °C	> 99	81
8	PhI(OAc) ₂	30 °C	70	74

^[a] Reaction conditions : catalyst (metal content : 2 mol%), substrate (0.5 mmol), PhI(OAc)₂ (1.5 mmol), 1,2-dichloromethane (5 mL) and water (0.5 mL), air (1 atm). Conversion and selectivity were calculated by GC and GC-MS with internal standard 1,4-biphenyl.

[18], and *t*-BuOOH[19,20] as oxidants. While conceding the inputs added by the previous work, some shortcomings are still required to be resolved such as safety issues concerned with ozone generation and industrially undesirable use of over stoichiometric quantities of oxidants has incited researchers to build up catalytic metal-based systems. Among them, ruthenium based catalysts has demonstrated a good selectivity towards the oxidative transformation of unsaturated hydrocarbons.

In the present study, we have reported Ru(OH)_x/ZrO₂ as an immediate economical and environmentally benign option for the selective oxidative transformation of alkenes or alkynes to aldehydes, diketones, or carboxylic acids. The catalyst has shown a sound activity in chlorinated solvents like dichloromethane and 1,2-dichloroethane after testing in various kinds of solvents and an efficient yield has been obtained by using (diacetoxyiodo)benzene (PhI(OAc)₂).

2. Experimental

2.1. Instruments and materials

Younglin GC-6500 instrument using a flame ionization detector (FID) equipped with a HP-INNOWAX capillary column (internal diameter = 0.25 mm, length = 30 m) was used to analyze the substrates and products. Mass spectra (GC/MS) were recorded on Hewlett Packard 6850 gas chromatograph system with 5973 MSD (Hewlett Packard, USA) at an ionization voltage of 70 eV equipped with a DB-5 capillary column (internal diameter = 0.25 mm, length = 30 m). An inductively coupled plasma emission spectrometer (ICP, Shimadzu ICPS-7510) conducted elemental analysis for transition metals. Substrates and reagents were purchased from Tokyo Chemical Industry Inc. and Sigma-Aldrich. Support ZrO₂ powder (BET surface area: 33 m²g⁻¹) was gained from Aldrich. Without further purification, all other reagents and solvents were used as received.

2.2. General procedure

The heterogeneous ruthenium zirconia catalyst, Ru(OH)_x/ZrO₂, was synthesized by our previous reported procedure[21]. Alkenes or alkynes oxidative cleavage reaction was conducted by using 2 mol% of Ru(OH)_x/ZrO₂, 0.5 mmol of substrates, and 5 mL of dichloromethane and 0.5 mL of deionized water with PhI(OAc)₂. The reaction was carried out in tubular type of reactors, equipped with cross-shaped mag-

netic stirrer at 30 °C. After reaction, each reaction solution was diluted by dichloromethane and water with 0.01 mmol of internal standard (biphenyl), and analyzed by gas chromatography (GC) and GC/MS.

2.3. Recycling test

Reusability test was carried out with 2 mol% of the catalyst Ru(OH)_x/ZrO₂, 0.5 mmol of cis-1,2-diphenylethylene, and 5 mL of dichloromethane and 0.5 mL of deionized water with PhI(OAc)₂ under 1 atm of air condition. The reaction was performed in tubular type reactors with cross-shaped magnetic bar at 30 °C. After the reaction, Ru(OH)_x/ZrO₂ catalyst was separated by filtration, and washed with deionized water and aqueous sodium hydroxide (0.1 M) and dried in *vacuo* for a while before being recycled.

3. Results and Discussion

3.1. Choice of catalyst

Various catalysts based on the transition metals such as ruthenium, iron, manganese, cobalt, or molybdenum have been used for the oxidative transformation of olefins and alkynes to aldehydes and ketones[22]. Among them, ruthenium has been used extensively in combination with the other compounds such as hydroxides, chlorides, various solid supports and ligands. In the given protocol, different ruthenium compounds were tested as catalyst for the selectivity and conversion of cis-stilbene to desired product (Table 1). Along with our presented heterogeneous catalyst, Ru(OH)_x/ZrO₂, several ruthenium based catalysts such as Ru(OH)_x/MgO, RuCl₃ · xH₂O, RuO₂, [Ru(*p*-cymene)Cl₂]₂ and Ru₃(CO)₁₂ were tested. Although they showed a good conversion of the substrate into the product but the selectivity towards the desired product was less as compared to our heterogeneous catalyst, Ru(OH)_x/ZrO₂.

3.2. Effect of solvent

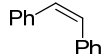
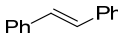


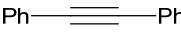
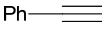
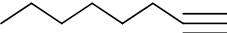
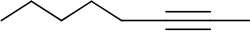

Oxidation reactions are highly influenced by the choice of solvent used during the oxidation process[5]. The solvent effect was explored by using the substrate of cis-stilbene as described before. The oxidation process was carried out by using two-phase solvents in the ratio of 5 mL/0.5 mL (organic/aqueous phase). Following solvents were used in the given ratio: 1,2-dichloromethane/water, acetonitrile/water,

Table 2. Results of Several Solvents Catalyzed by Ru(OH)_x/ZrO₂ with Water^[a]

Entry	Solvent	Conv. (%)	Select. (%)
1	1,2-dichloromethane	> 99	93
2	acetonitrile	99	59
3	isopropyl alcohol	2	>99
4	THF	39	62
5	ethyl acetate	> 99	77
6	1,4-dioxane	> 99	70
7	acetone	> 99	70
8	1,2-dichloroethane	> 99	86
9 ^[b]	only water	> 99	33

^[a] Reaction conditions : Ru(OH)_x/ZrO₂ (Ru : 2 mol%), cis-1,2-diphenylethylene (0.5 mmol), PhI(OAc)₂ (1.5 mmol), solvent (5 mL) and water (0.5 mL), air (1 atm). Conversion and selectivity were determined by GC and GC-MS analyses with internal standard 1,4-biphenyl. ^[b] Only water was used as a solvent (5.5 mL).

Table 3. Oxidative Cleavage Catalyzed by Ru(OH)_x/ZrO₂ with Various Alkenes or Alkynes^[a]

Entry	Substrate	Yield (%)	Condition
1		PhCHO (93) PhCOOH (85)	A B
2		PhCHO (90) PhCOOH (98)	A B
3		PhCOOH (78)	B
4		PhCHO (57), PhCOOH (20) PhCOOH (70), PhCOCOCH ₃ (25)	A B
5		PhCOCOPh (80), PhCOOH (20) PhCOCOPh (63), PhCOOH (32)	A B
6		PhCOOH (53), PhCOCHO (25) PhCOOH (83)	A B
7		C ₆ H ₁₃ COOH (92)	B
8		C ₅ H ₁₁ COCOCH ₃ (51), C ₅ H ₁₁ COOH (24)	B
9		HOOC(CH ₂) ₄ COOH (97)	B

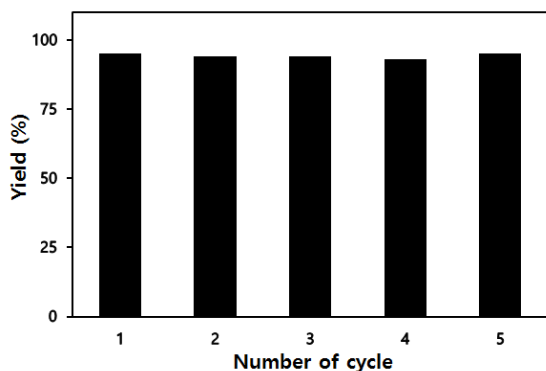
^[a] Reaction conditions : condition A for substrate (0.5 mmol), Ru(OH)_x/ZrO₂ (2 mol%), PhI(OAc)₂ (1.5 mmol), dichloromethane (5 mL), water (0.5 mL), 30 °C, and air (1 atm) in 5 min. Condition B for Ru(OH)_x/ZrO₂ (3 mol%), PhI(OAc)₂ (2.5 mmol), and 1.5 h. Using GC and GC-MS instruments, all yields were calculated with internal standard 1,4-biphenyl.

isopropyl alcohol/water, THF/water, ethyl acetate/water, 1,4-dioxane/water, and 1,2-dichloroethane/water, and only water (Table 2). It can be seen from the experimental data that oxidative transformation of the cis-1,2-diphenylethylene demonstrated low conversion and selectivity in all cases as solvent systems, except 1,2-dichloromethane/water with high yield. The 1,2-dichloromethane (5 mL)/water (0.5 mL) was proved to be the best solvent in view of > 99% conversion of cis-stilbene and 93% yield of aldehyde in 5 min (Table 2, entry 1).

3.3. Oxidative cleavage of terminal or internal olefins

Under the optimum conditions employing the heterogeneous Ru(OH)_x/ZrO₂ catalyst (2 mol%) and 1,2-dichloromethane/water (5 mL/ 0.5 mL) solvent system in the presence of PhI(OAc)₂ (1.5 or 2.5

mmol) as oxidant, various terminal and internal olefins were subjected to oxidative cleavage (Table 3, entries 1 to 4 and 9). It can be seen from the Table 3 that the prescribed heterogeneous system showed different products under conditions (A or B). The reaction was completed in 5 min. in condition (A) while in condition (B) it took 1.5 h. GC-MS analysis was carried out to calculate the percentage conversion and selectivity by using 1,4-biphenyl as internal standard. According to the results, terminal alkenes (entry 3) and the aliphatic cyclic alkene (entry 9) gave the acid product in large percentage instead of giving aldehyde as major product, 78% and 97%, respectively. These product yields can be attributed by the prolonged reaction time, i.e. 1.5 h leading towards the over oxidation of the substrate and converting it into acid product without stopping at aldehyde stage. However, the internal alkenes (entries 1, 2, and 4) not only showed the over oxidation product



^[a] Reaction conditions: catalyst (2 mol%), 0.5 mmol of cis-1,2-diphenylethylene, PhI(OAc)₂ (1.5 mmol), dichloromethane (5 mL) and water (0.5 mL), air (1 atm). Percentages for conversion and selectivity by GC and GC-MS analyses with internal standard 1,4-biphenyl.

Figure 1. Recycling result of Ru(OH)_x/ZrO₂ catalyst for alkene oxidative cleavage reaction^[a].

(carboxylic acid) under condition B but also a relatively good to excellent yield of the major product (aldehyde) under condition A. The diketone was obtained in entry 4 under condition B as a minor product.

3.4. Oxidative cleavage of various alkynes and reusability of the catalyst

Oxidation of alkynes is accompanied with very useful products named as diketones. Diketones are not only an efficient natural compound but they also act as an inhibitor in steel corrosion and photo-sensitive material in photo-curable coatings[23,24]. A lot of biologically active heterocyclic compounds can be synthesized by using diketones as intermediate. Though some disadvantages like rigorous reaction conditions, prolonged reaction time and low yield are associated with the formation of diketones but these problems can be resolved by using high concentration of oxidant or some new catalyst[25]. In this study, different substrates were subjected to oxidation under two reaction conditions and the results are shown in the Table 3 (entries 5 to 8). It can be seen that only the internal alkynes (entries 5 and 8) yielded the diketone as the major product, i.e. 80% and 51% respectively. The terminal alkynes from (entries 6 and 7) yielded carboxylic acids as major products instead of diketones. This can be attributed to the fact that terminal alkynes are more prone to be converted into carboxylic acids under prolonged reaction conditions. The Ru(OH)_x/ZrO₂ catalyst could be simply eliminated from the reaction mixture using only filtration process. The same reaction with the reused catalyst was recycled 5 times without significant loss of its original catalytic performance (Figure 1). There is no detection of ruthenium species by ICP-AES analysis from the reaction supernatant.

4. Conclusions

In summary, a direct and efficient heterogeneous catalyst system for the selective oxidative scission of alkenes or alkynes to aldehydes, diketones, or carboxylic acids has been demonstrated. This method has

proved to be a good alternative to previous shortcomings in the transformation process. The current catalyst (Ru(OH)_x/ZrO₂) afforded good to excellent yields of the products under varying reaction conditions in the presence of oxidant (diacetoxyiodo)benzene and dichloromethane/water solvent system at 30 °C for a wide range of substrates. The recycle test results exhibited that the proposed catalyst can be used for the oxidative scission process for several times without any conspicuous change in its catalytic activity. These features make this method attractive for practical applications.

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