Solvent-Free Oxidative Coupling of 2-Naphthols Catalyzed by Hydrotalcite-Like Compounds in Aerobic Conditions

Kazuhiro Sugamoto*, Yoh-ichi Matsushita and Takanao Matsui

Faculty of Engineering, University of Miyazaki, Gakuen-Kibanadai, Miyazaki 889-2192, Japan Received March 30, 2011: Revised April 27, 2011: Accepted January 31, 2012

Abstract: The hydrotalcite-like compound having ruthenium ions, cobalt ions, and iron ions in the Brucite layer and CO_3 anions in the interlayer (Ru-Co-Fe-CO₃ HTLC) was found to be effective heterogeneous catalyst for the solvent-free oxidative coupling of 2-naphthols in aerobic conditions. The catalyst could be easily recovered and reused repeatedly for the reaction.

Keywords; 1,1'-bi-2-naphthols, 2-naphthol, green chemistry, heterogeneous catalysis, oxidation, solid-phase synthesis.

INTRODUCTION

1,1'-Bi-2-naphthols have been widely used as chiral auxiliaries on various asymmetric reactions [1]. The synthesis of 1,1'-bi-2-naphthols has been attempted via the oxidative coupling reaction of 2-naphthols using various homogeneous metal catalyst, such as Cu(II) amine complex [2], VO(acac)₂ [3], copper Schiff base complex [4], methyloxorhenium [5], and V₂O₅ [6]. Recently, CuSO₄/Al₂O₃ [7], Cu-exchanged montmorillonite [8], FeCl₃/Al₂O₃ [9], Cu/MCM-41 [10], V/MCM-41 [11], Ru(OH)_x/Al₂O₃ [12], Fe impregnated pillared montmorillonite K10 [13], and biopolymer supported Cu(II) catalyst [14] have been used for heterogeneous catalysts on the oxidative coupling of 2naphthols. Although these methods require solvent, the use of heterogeneous catalysts offers several advantages over homogeneous ones, such as ease of recovery and recycling and atom utility. Hydrotalcite-like compounds (HTLCs) are reported to be a turnable heterogeneous catalyst for various organic reactions [15]. We report herein a solvent-free oxidative coupling of 2-naphthols catalyzed by HTLCs in aerobic conditions.

We first examined the effect of several types of HTLCs (150 mg) on solvent-free oxidative coupling of 2-naphthol (1, 1 mmol) at 50 °C for 24h in aerobic conditions. The results are summarized in Table 1. All HTLCs were prepared according to a procedure in the literature [15d]. The reaction of 1 using HTLC having cobalt ions and iron ions in the Brucite layer and CO₃ anions in the interlayer (Co-Fe-CO₃ HTLC) and Cu-Fe-CO₃ HTLC gave the 1,1'-bi-2-naphthol (2) in low yield (Entries 1 and 2). The Ru-Co-Fe-CO₃ HTLC containing small amounts of ruthenium ions was the most effective catalyst (Entry 3). On the other hand, substitution of iron ions with aluminum ions (Ru-Co-Al-CO₃ HTLC) and ruthenium ions with rhodium ions (Rh-Co-Fe-CO₃ HTLC) in Brucite layer were not effective (Entries 4 and 5).

Next, we tried recovery and reuse of Ru-Co-Fe-CO₃ HTLC on the solvent-free oxidative coupling of 1 at 50 °C

for 24 h in aerobic conditions (Table 2). After the reaction, 5 ml of EtOAc was added to the reaction mixture. The catalyst was separated by filtration, and washed with 5 ml of EtOAc. The separated catalyst was dried *in vacuo* before recycling. The recovered catalyst was used for successive runs. The activity of recovered catalyst decreased after the catalyst had been used several times (Entry 3). Matsushita *et al.* reported the recovered HTLC was washed with 10% sodium carbonate aqueous solution and then water, which could be reused as a catalyst without an appreciable loss of activity for the oxidation of alcohol catalyzed by Ru-Co-Al-CO₃ HTLC [15d]. Similarly, the activation of the catalyst was recovered when the recovered catalyst was washed with same manner (Entry 4).

The present reaction was applied to preparation of several binaphthols (Table **3**). The solvent-free oxidative coupling of 6-bromo-2-naphthol and 8-methoxy-2-naphthol in aerobic conditions gave corresponding binaphthols in low yields at 50 °C for 24 h, respectively (Entries 1 and 4). Increasing reaction temperature afforded binaphthols in 89% yield at 100 °C and 98% yield at 80 °C, respectively (Entries 3 and 5). The oxidative coupling of 2,6-di-*tert*-butylphenol and 2,4-di-*tert*-butylphenol at 50 °C for 24 h gave 3,3',5,5'-tetra-*tert*-butyl-4,4'-diphenoquinone and 3,3',5,5'-tetra-*tert*-butyl-2,2'-biphenyldiol in 96% yields, respectively (Entries 6 and 7).

In conclusion, solvent-free oxidation coupling of 2naphthols catalyzed by Ru-Co-Fe-CO₃ HTLC in aerobic conditions gave binaphthols in good yields. From the standpoint of green chemistry and technology, the present reaction has the following significant advantages: (i) solventfree reaction, (ii) the use of air as solo oxidant, (iii) heterogeneous catalyst, (iv) simple workup procedures, (v) reusability of catalyst.

EXPERIMENTAL

Typical Procedure

A mixture of 1 (144 mg, 1 mmol) and Ru-Co-Fe-CO₃ HTLC (150 mg) was stirred by stirring bar at 50 °C for 24 h. After the reaction, 5 ml of EtOAc was added to the reaction

^{*}Address correspondence to this author at the Faculty of Engineering, University of Miyazaki, Gakuen-Kibanadai, Miyazaki 889-2192, Japan; Tel +81-985-58-7390; Fax: +81-985-58-7323;

E-mail: sugamoto@cc.miyazaki-u.ac.jp

Solvent-Free Oxidative Coupling of 2-Naphthol Catalyzed by Various HTLCs in Aerobic Conditions Table 1.



Entry	HTLC (Molar ratio)	Yield of 1/% ^{a)}	Recov. of 2/% ^{a)}
1	Co-Fe-CO ₃ HTLC (Co/Fe = $3.0/1.3$)	21	72
2	Cu-Fe-CO ₃ HTLC (Cu/Fe = $3.0/1.3$)	16	69
3	Ru-Co-Fe-CO ₃ HTLC (Ru/Co/Fe = 0.1/ 3.0/1.0)	86	0
4	Ru-Co-Al-CO ₃ HTLC (Ru/Co/Al = 0.1/ 3.0/1.0)	37	58
5	Rh-Co-Fe-CO ₃ HTLC (Rh/Co/Fe = $0.1/3.0/1.0$)	8	78

^aIsolated yield.

Repeated Use of Ru-Co-Fe-CO₃ HTLC for the Solvent-Free Oxidative Coupling of 2-Naphthol Table 2.



Run	Yield of 2/% ^{a)}	Recov. of 1/% ^{a)}	Recov. of catalyst/%	
1	90	0	102	
2	80	8	94	
3	46	47	95	
4 ^{b)}	94	0	95	
5	79	16	95	

^aDetermined by GC. ^bThe recovered catalyst from the reaction of run 3 was washed with 10% sodium carbonate aqueous solution and then water. The washed catalyst was dried at rt *in vacuo* and used on

Table 3. Solvent-Free Oxidative Coupling of Substituted 2-Naphthols and Di-Tert-Butylphenols Catalyzed Ru-Co-Fe-CO3 HTLC in Aerobic Conditions for 24 h

Entry	Substrate	Temp./ °C	Product	Yield/% ^{a)}	Recov./% ^{a)}
1		50	Br	53	47
2	Br,	80		77	18
3		100	ОН	89	0
	ОН		Br		





^aIsolated yield.

mixture. The catalyst was separated by filtration, and washed with 5 ml of EtOAc. The separated catalyst was dried *in vacuo* before recycling. The filtrate was concentrated under reduced pressure to afford the crude product. The product was purified by silica gel column chromatography with hexane- EtOAc to give 2 (123 mg) in 86% yield. Similarly other compounds were oxidized using this procedure and their conditions are given in the Table 3. The products were identified by comparing their physical and spectral data with those of authentic compounds reported in literature [7, 16].

CONFLICT OF INTEREST

Declared none.

ACKNOWLEDGEMENT

Declared none.

REFERENCES

- For selected reviews, see: (a) Kagan, H. B.; Riant, O. Catalytic asymmetric Diels Alder reactions. *Chem. Rev.*, **1992**, *92*, 1007-1019. (b) Mikami, K.; Shimizu, M. Asymmetric ene reactions in organic synthesis. *Chem. Rev.*, **1992**, *92*, 1021-1050.
- [2] Noji, M.; Nakajima, M.; Koga, K. A new catalytic system for aerobic oxidative coupling of 2-naphthol derivatives by the use of CuCl-amine complex: A practical synthesis of binaphthol derivatives. *Tetrahedron Lett.*, **1994**, *35*, 7983-7984.
- [3] Hwang, D. -R.; Chen, C. -P.; and Uang, B. -J. Aerobic catalytic oxidative coupling of 2-naphthols and phenols by VO(acac)₂. *Chem. Commun*, **1999**, 1207-1208.
- [4] Chu, C. -Y.; Hwang, D. -R.; Wang, S. -K.; Uang, B. -J. Chiral oxovanadium complex catalyzed enantioselective oxidative coupling of 2-naphthols. *Chem. Commun*, 2001, 980-981.

- [5] Sharma, V. B.; Jain, S. L.; Sain, B. Methyltrioxorhenium-catalyzed aerobic oxidative coupling of 2-naphthols to binaphthols. *Tetrahedron Lett.*, 2003, 44, 2655-2656.
- [6] Joseph J. K.; Jain S. L., Sain B. V₂O₅-O₂ as a simple and efficient protocol for the oxidative coupling of 2-naphthols to binaphthols under mild reaction conditions. *J. Org. Chem.*, **1994**, *59*, 6859-6861.
- [7] Sakamoto, T.; Yonehara, H.; Pac, C. Efficient oxidative coupling of 2-naphthols catalyzed by alumina-supported copper(II) sulfate using dioxygen as oxidant. J. Org. Chem., 1994, 59, 6859-6861.
- [8] Kantam M. L.; Santhi, P. L. Oxidative coupling of 2-naphthols catalysed by Cu-exchanged montmorillonite. *Synth. Commun.*, **1996**, 26, 3075-3079.
- [9] Li, T. -S.; Duan, H. -Y.; Li, B. -Z.; Tewari, B. B.; Li, S. -H. Novel oxidative coupling of 2-naphthols to 1,1'-bi-2-naphthols catalysed by solid Lewis acids using atmospheric oxygen as oxidant. J. Chem. Soc. Perkin Trans. 1, 1999, 291-293.
- [10] Prasad, M. R.; Kamalakar, G.; Kulkarni, S. J.; Raghavan, K.V. Synthesis of binaphthols over mesoporous molecular sieves. J. Mol. Cat. A: Chem., 2002, 180, 109-123.
- [11] Ikeda, T.; Misawa, N.; Ichihashi, Y.; Nishuyama, S.; Tsuruya, S. Liquid-phase oxidative coupling of 2-naphthol by vanadium catalysts supported on MCM-41. J. Mol. Cat. A: Chem., 2005, 231, 235-240.
- [12] Matsushita, M.; Kamata, K.; Yamaguchi, K.; Mizuno, N. Heterogeneously catalyzed aerobic oxidative biaryl coupling of 2naphthols and substituted phenols in water. J. Am. Chem. Soc., 2005, 127, 6632-6640.
- [13] Bhor, M. D.; Nandurkar, N. S.; Bhanushali, M. J.; Bhanage, B. M. An efficient oxidative coupling of naphthols catalyzed by Fe impregnated pillared montmorillonite K10. *Catal. Lett.*, **2006**, *112*, 45-50.
- [14] Reddy, K. R.; Rajgopal, K.; Kantam, M. L. Copper-alginates: A biopolymer supported Cu(II) catalyst for 1,3-dipolar cycloaddition of alkynes with azides and oxidative coupling of 2-naphthols and phenols in water. *Catal. Lett.*, **2007**, *114*, 36-40.
- [15] Examples of organic reactions catalyzed by hydrotalcite-like compounds: (a) Choudary, B. M.; Narender, N.; Bhuma, V. A novel hydroperoxidzation of alkanes using calcined ZnCrCO₃-HTlc. *Synlett*, **1994**, 641-642. (b) Auer, S. M.; Schneider, M.; Baiker, A. Novel heterogeneous route for the coupling of phenylethyne by a catalyst derived from Cu-Mg-Al hydrotalcite. *J. Chem. Soc., Chem. Commun.*, **1995**, 2057-2058. (c) Kaneda, K.;

Yamashita, T.; Matshushita, T.; Ebitani, K. Heterogeneous Oxidation of Allylic and benzylic alcohols catalyzed by Ru-Al-Mg hydrotalcites in the presence of molecular oxygen. *J. Org. Chem.*, **1998**, *63*, 1750-1751. (d) Matsushita, T.; Ebitani, K.; Kaneda, K. Highly efficient oxidation of alcohols and aromatic compounds catalysed by the Ru-Co-Al hydrotalcite in the presence of molecular oxygen. *Chem. Commun.*, **1999**, 265-266. (e) Choudary, B. M.; Kantam, M. L.; Rahman, A.; Reddy, C. V.; Rao, K. K. The first example of activation of molecular oxygen by nickel in ni-al hydrotalcite: A novel protocol for the selective oxidation of alcohols. *Angew. Chem. Int. Ed.*, **2001**, *40*, 763-766. (f) Kawabata,

T.; Fujisaki, N.; Shishido, T.; Nomura, K.; Sano, T.; Takehira, K. Steam reforming of dimethyl ether over ZSM-5 coupled with Cu/ZnO/Al₂O₃ catalyst prepared by homogeneous precipitation. J. Mol. Cat. A: Chem., **2006**, 253, 279-289. (g) Alvarez, M. G.; Segarra, A. M.; Conteras, S.; Sueiras, J. E.; Medina, F.; Figueras, F. Enhanced use of renewable resources: Transesterification of glycerol catalyzed by hydrotalcite-like compounds. Chem. Engineer. J., **2010**, *161*, 340-345.

[16] Gupta, R; Mukherjee, R. Catalytic oxidation of hindered phenols by a copper(I) complex and dioxygen *Tetrahedron Lett.*, **2000**, *41*, 7763-7767.