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Heterogeneously Catalyzed Aerobic Oxidative Biaryl Coupling of 2-Naphthols and Substituted Phenols in Water

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Abstract: The oxidative coupling reaction can efficiently be promoted by supported ruthenium catalyst $Ru(OH)_x/Al_2O_3$. A variety of 2-naphthols and substituted phenols can be converted to the corresponding biaryl compounds in moderate to excellent yields using molecular oxygen as a sole oxidant in water without any additives. The catalysis is truly heterogeneous in nature, and $Ru(OH)_x/Al_2O_3$ can easily be recovered after the reaction. The catalyst can be recycled seven times with the maintenance of the catalytic performance, and the total turnover number reaches up to 160. The results of competitive coupling reactions suggest that the present oxidative biaryl coupling reaction proceeds via the homolytic coupling of two radical species and the $Ru(OH)_x/Al_2O_3$ catalyst acts as an one-electron oxidant. Two radical species are coupled to give the corresponding biaryl product, and the one-electron reduced catalyst is reoxidized by molecular oxygen. The amounts of O_2 uptake and H_2O formation were almost one-quarter and one-half the amount of substrate consumed, respectively, supporting the reaction mechanism. The kinetic data and kinetic isotope effect show that the reoxidation of the reduced catalyst is the rate-limiting step for the coupling reaction.

Introduction

The syntheses of the biaryl compounds are of importance because they are used as building blocks of many alkaloids and natural products, auxiliaries, and ligands for a wide range of organic functional transformations.[1] Especially, homochiral 1,1′-binaphthalene derivatives have successfully been utilized as chiral inducers for stereo- and enantioselective reactions because of their axial dissymmetry and molecular flexibility.[2] Therefore, much attention has been paid to the development of efficient syntheses of 1,1′-binaphthalene-2,2′-diol (BINOL) derivatives, which are versatile sources of the various 1,1′-binaphthalene skeletons. The oxidative coupling of 2-naphthols is one of the most useful methods for the syntheses of BINOL derivatives. Although various kinds of stoichiometric oxidation reagents such as Fe, Cu, Mn, and Ti salts have been employed for the reaction,[3] they are often hazardous, expensive, stoichiometric, and difficult to remove from the reaction solution.

In the laboratory scale synthesis as well as the manufacture of large-volume petrochemicals, the environmentally unacceptable processes should be replaced by "greener" catalytic ones with clean, safe, and inexpensive oxidant of molecular oxygen. While some efficient catalytic procedures using molecular oxygen as a sole oxidant for the above reaction have been developed,[4−6] most of them are homogeneous systems, and there are few heterogeneous catalysts despite their significant advan-

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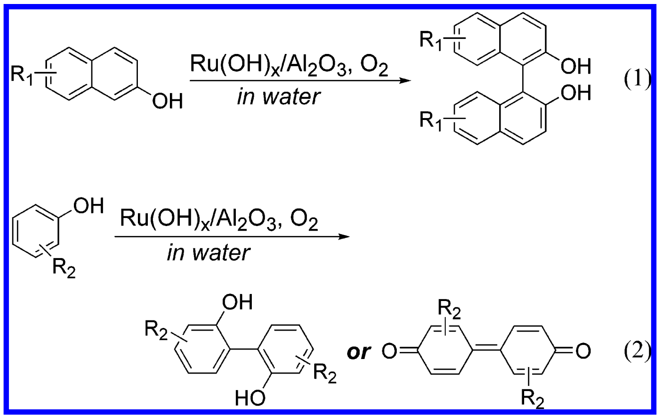
tages from environmental and economical standpoints, easy separation from the reaction mixture, and recycling of catalysts.[7] Cu^{2+}-exchanged MCM-41,[5a,b] Fe^{3+}-exchanged MCM-41,[5b] Fe^{3+}-exchanged montmorillonite,[5c] Cu^{2+}-exchanged montmorillonite,[5d] $CuSO_4/Al_2O_3$,[5e] K/Cu−Mg−Al−CO_3 hydrotalcite,[5f] and vanadium-Shiff-base/SiO_2[6i] are examples of the heterogeneous catalysts for the oxidative biaryl coupling reaction. However, the reported heterogeneous systems have disadvantages: (i) Turnover numbers are still low (≤33), (ii) the catalysts are deactivated, (iii) forced reaction conditions (≥403 K) are required to attain high yield of products, and/or (iv) these reactions are typically performed in environmentally undesirable halogenated organic solvents such as chlorobenzene and chloroform.

Recently, organic reactions in water are of great interest[8] because water is much safer than the usual organic solvents, which are often inflammable, explosive, and carcinogenic, and can diminish the pollution problems. The separation and recovery of catalysts and products can be achieved by the phase separation and/or extraction with some loss of catalysts and products (in some cases). These properties make the use of water favorable not only in laboratory-scale organic syntheses but also in industries. Many water-soluble ligands have now been developed for transition metal-catalyzed reactions in water.[8] Phase-transfer agents and surfactants are also used to retain contact between hydrophobic substrates and the catalyst in the water phase.[8]

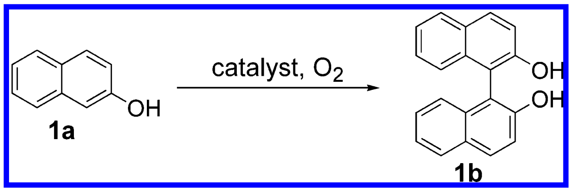
In this paper, we report that the supported ruthenium hydroxide catalyst ($Ru(OH)_x/Al_2O_3$) is found to act as an effective heterogeneous catalyst for the aerobic biaryl coupling of 2-naphthols and substituted phenols in water without any additives (eqs 1 and 2). $Ru(OH)_x/Al_2O_3$ can easily be separated by the filtration and reused several times with retention of the high catalytic activity. The catalysis is truly heterogeneous in nature because the filtrate after removal of the solid catalyst is completely inactive. As far as we know, the heterogeneous catalytic aerobic biaryl coupling reactions of 2-naphthols and substituted phenols in water have never been reported so far. Furthermore, we investigate the reaction mechanism of the present oxidative coupling reaction in detail.



Results and Discussion

$Ru(OH)_x/Al_2O_3$-Catalyzed Oxidative Biaryl Coupling in Water. First, the oxidative coupling of 2-naphthol (**1a**) was carried out using $Ru(OH)_x/Al_2O_3$ at 353 K under 1 atm of molecular oxygen in various solvents. The results are summarized in Table 1. The reaction did not proceed at all without $Ru(OH)_x/Al_2O_3$. The use of nonpolar solvents of toluene and 1,2-dichloroethane gave the corresponding BINOL (**1b**) in high yields (entries 2 and 3), and polar organic 1,2-dimethoxyethane, acetonitrile, and ethanol were poor solvents (entries 4−6). It was found that water was also an effective solvent for the present oxidative coupling with $Ru(OH)_x/Al_2O_3$, 50% yield of **1b** at 51% conversion of **1a** under the conditions (entry 1). In this case, no byproducts such as perylenes, quinones, and polymers could be detected by ^1H and ^{13}C NMR analyses of the crude reaction mixture. Because the use of organic solvents such as toluene and 1,2-dichloroethane is undesirable from an environmental point of view and the highest selectivity was observed in water, we hereafter used water as a solvent.

Table 1. Oxidative Coupling of **1a**[a]



entry	catalyst	solvent	conv. of **1a**[b] (%)	yield of **1b**[b] (%)
1	$Ru(OH)_x/Al_2O_3$	water	51	50
2	$Ru(OH)_x/Al_2O_3$	toluene	99	84
3	$Ru(OH)_x/Al_2O_3$	1,2-dichloroethane	87	78
4	$Ru(OH)_x/Al_2O_3$	1,2-dimethoxyethane	24	19
5	$Ru(OH)_x/Al_2O_3$	acetonitrile	18	12
6	$Ru(OH)_x/Al_2O_3$	ethanol	<1	
7	$Ru(OH)_x/TiO_2$	water	44	26
8	$Ru(OH)_x/SiO_2$	water	7	5
9	$Cu(OH)_x/Al_2O_3$	water	76	60
10	$Fe(OH)_x/Al_2O_3$	water	8	8
11	$Pd(OH)_x/Al_2O_3$	water	<1	
12	$Rh(OH)_x/Al_2O_3$	water	<1	
13	$RuCl_3 \cdot nH_2O$	water	39	32
14	$RuCl_2(bpy)_3$	water	<1	
15	$[RuCl_2(p\text{-cymene})]_2$	water	14	7
16	RuO_2 (anhydrous)	water	<1	
17	$Ru(OH)_x \cdot nH_2O$	water	10	10
18	$Ru(OH)_x \cdot nH_2O + Al_2O_3$[c]	water	11	9
19	$CuCl_2$	water	32	4
20	Al_2O_3[c]	water	<1	
21	none	water	<1	

[a] Reaction conditions: **1a** (0.3 mmol), catalyst (metal: 5 mol %), solvent (1.5 mL), 353 K, 2 h, under 1 atm of molecular oxygen. [b] Conversions and yields were determined by ^1H NMR analyses of the crude reaction mixture and based on **1a**. [c] Al_2O_3 (64 mg).

Next, the catalytic activities of the oxidative coupling of **1a** in water were compared with various catalysts (Table 1).

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$Ru(OH)_x/Al_2O_3$ and $Cu(OH)_x/Al_2O_3$ gave **1b** in 50% and 60% yields, respectively (entries 1 and 9). No reaction proceeded in the presence of Al_2O_3 (entry 20), showing that supported transition metals such as ruthenium and copper are active species for the coupling reaction. The homogeneous $RuCl_3 \cdot nH_2O$ and $CuCl_2$ catalysts showed moderate catalytic activities (entries 13 and 19), but they were lower than those of $Ru(OH)_x/Al_2O_3$ and $Cu(OH)_x/Al_2O_3$. The Ru^{2+} complexes such as $RuCl_2(bpy)_3$ and $[RuCl_2(p\text{-cymene})]_2$ were not effective for the reaction (entries 14 and 15). RuO_2 (anhydrous) showed no catalytic activity (entry 16), while 10% yield of **1b** was obtained in the case of $Ru(OH)_x \cdot nH_2O$ (entry 17). It is noted that the catalytic activity of a mixture of $Ru(OH)_x \cdot nH_2O$ and Al_2O_3 powders was comparable to that of $Ru(OH)_x \cdot nH_2O$ and much lower than that of $Ru(OH)_x/Al_2O_3$ (entry 18), indicating that the supporting ruthenium hydroxide species on Al_2O_3 is essential for the appearance of the high activity of $Ru(OH)_x/Al_2O_3$ in water. The $Ru(OH)_x/TiO_2$ and $Ru(OH)_x/SiO_2$ were less active than $Ru(OH)_x/Al_2O_3$ (entries 7 and 8).

The catalytic activity (yield of **1b**) of transition metal hydroxide catalysts supported on Al_2O_3 decreased in the order of $Cu(OH)_x$ (60%) > $Ru(OH)_x$ (50%) > $Fe(OH)_x$ (8%) ≫ $Pd(OH)_x$ (<1%), $Rh(OH)_x$ (<1%), and $Cu(OH)_x/Al_2O_3$ gave the highest yield of **1b**. The catalytic activity decreased with an increase in the redox potential of the transition metal ions, Cu^{2+}/Cu^{+} (0.15 V vs SHE), Ru^{3+}/Ru^{2+} (0.25 V), Fe^{3+}/Fe^{2+} (0.77 V).[9] Unidentified byproducts were formed at higher conversion of **1a** in the case of $Cu(OH)_x/Al_2O_3$, resulting in low selectivity to **1b**; when the oxidative coupling was carried out with $Cu(OH)_x/Al_2O_3$ under the conditions in Table 2, only 66% yield of **1b** was obtained at >99% conversion of **1a**. Further, copper species were leached into the reaction solution to some extent (~7%) under the conditions, and the recovered $Cu(OH)_x/Al_2O_3$ catalyst was less active than the fresh catalyst.[10] In contrast, no leaching of ruthenium species was observed, and the recovered catalyst after the reaction could be reused without loss of the catalytic activity in the case of $Ru(OH)_x/Al_2O_3$ (see below). Therefore, the oxidative coupling reactions hereafter were carried out with $Ru(OH)_x/Al_2O_3$ in water.

It is important to verify that the observed catalysis is caused by solid $Ru(OH)_x/Al_2O_3$ or leached ruthenium species. Therefore, the following control experiment was carried out. A catalytic oxidative coupling of **1a** was carried out under the conditions in Table 2, and $Ru(OH)_x/Al_2O_3$ and product **1b** were removed from the reaction mixture by the filtration at the reaction temperature after complete consumption of **1a**. The substrate **1a** (0.3 mmol) was again added to the filtrate, and the mixture was heated at 373 K. No conversion of **1a** was observed. As above-mentioned, no ruthenium species was present in the reaction solution (ICP-AES analysis, below the detection limit of 7 ppb). Moreover, the first-order dependence of the reaction rate on the amount of $Ru(OH)_x/Al_2O_3$ (Ru: ~6.5 mol %, Figure 1) was observed. These observations can rule out any contribution to the observed catalysis from ruthenium species that leached into the reaction solution, and the observed catalysis is truly heterogeneous in nature.[11]

The scope of the present $Ru(OH)_x/Al_2O_3$-catalyzed oxidative coupling in water with regard to various kinds of 2-naphthols was examined. The results are summarized in Table 2. All of the products were isolated and fully characterized by comparison of the physical data with the authentic data. When the oxidation of **1a** was carried out at 373 K, the complete conversion of **1a** was achieved and 98% of **1b** was isolated after 4 h (entry 1). A larger-scale reaction (25-fold scaled up) showed the same results as for the small-scale experiments in Table 2. A mixture of **1a** (1.08 g, 7.5 mmol) and $Ru(OH)_x/Al_2O_3$ (Ru: 5 mol %) in 37.5 mL of water was heated at 373 K for 4 h, giving analytically pure **1b** in 97% isolated yield (1.04 g) after the recrystallization. Further, $Ru(OH)_x/Al_2O_3$ catalyst could be reused with the maintenance of the high catalytic performance; even in the seventh recycling run, **1a** was quantitatively converted to **1b** at the same reaction rate as that for the first run (Table 3). The turnover number (TON) for one run was 20, and the total TON reached up to 160 after the seventh recycling. The TONs (for one run) reported for other catalysts were as follows: CuCl(OH)/TMEDA (homogeneous, TON = 90),[4b] photoactivated $[Ru^{II}(salen)(NO)]$ (homogeneous, 48),[6g] vanadium-Schiff-base/SiO_2 (heterogeneous, 33),[6i] oxovanadium(IV) complex (homogeneous, 33),[6j] methyltrioxorhenium (homogeneous, 18),[4a] divanadium(IV) complex (homogeneous, 17),[6d] $CuSO_4/Al_2O_3$ (heterogeneous, 13),[5e] Cu^{2+}-exchanged MCM-41 (heterogeneous, 12),[5a] $VO(acac)_2$ (homogeneous, 10),[5h] $Mn(acac)_3$ (homogeneous, 9),[5h] dicopper(II) complex (homogeneous, 9),[6f] $RuCl_3$/[bimi]PF_6 (homogeneous, 9),[4d] Fe^{3+}-exchanged montmorillonite (heterogeneous, 7),[5c] Fe^{3+}-exchanged MCM-41 (heterogeneous, 3).[5b] It is noted that air can be used as an oxidant instead of molecular oxygen in the present system (entries 2 and 4). Also, the catalytic oxidative coupling of substituted 2-naphthols **2a**−**6a** efficiently proceeded to afford the corresponding BINOL derivatives **2b**−**6b** in moderate to high yields (entries 3−8). Deuterium labeled 2-naphthol **7a** was also oxidized to give the corresponding BINOL **7b** in excellent yield with almost the same reaction rate as that for **1a** (entry 9).

The present procedure was further applied to the oxidative coupling of substituted phenols. The product selectivities depended on the substitution pattern of phenols. For 2,4-di-*tert*-butylphenol (**8a**), the *ortho*−*ortho* coupling product **8b** was mainly obtained (entry 10). 2,6-Di-*tert*-butylphenol (**9a**) gave the *para*−*para* coupling product of diphenoquinone **9b** and a small amount of diphenol without formation of the corresponding benzoquinone (entry 11). In the case of 2,6-dimethylphenol (**10a**), the major product was diphenoquinone **10b** (entry 12). These high selectivities to the *para*−*para* coupling products for the oxidative coupling of 2,6-disubstituted phenols are very similar to those of the laccese and tyrosinase enzyme-catalyzed system, where Cu^{2+} acts as a one-electron oxidant to generate the radical species from the starting phenol and Cu^{+} is reoxidized by molecular oxygen.[12]

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[10] The $Cu(OH)_x/Al_2O_3$-catalyzed oxidative coupling of **1a** under the conditions in Table 2 gave 66% yield of **1b** at >99% conversion of **1a** (first run). In the recycling experiment using the recovered $Cu(OH)_x/Al_2O_3$, 41% yield of **1b** was obtained at 88% conversion of **1a** under the same reaction conditions.

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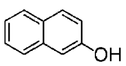
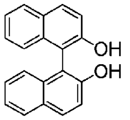
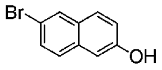
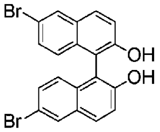
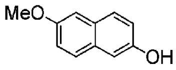
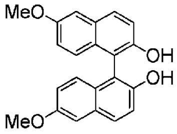
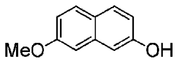
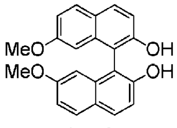
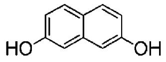
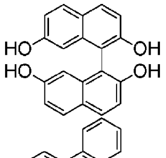
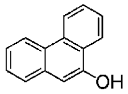
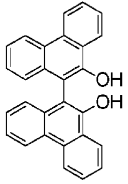
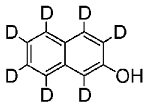
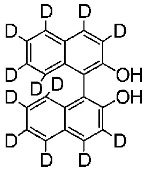
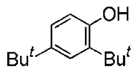
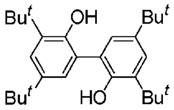
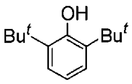
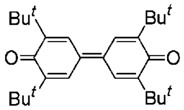
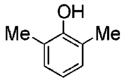
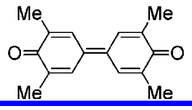
Table 2. Oxidative Coupling of 2-Naphthols and Substituted Phenols in Water Catalyzed by $Ru(OH)_x/Al_2O_3$[a]

Entry	Substrate	Time(h)	Conv.[b](%)	Product	Yield[c](%)
1 2[d]	 **(1a)**	4 5	>99 97	 **(1b)**	98 94
3 4[d]	 **(2a)**	6 9	>99 97	 **(2b)**	>99 95
5	 **(3a)**	4	>99	 **(3b)**	87
6	 **(4a)**	4	96	 **(4b)**	95
7	 **(5a)**	4	84	 **(5b)**	60[e]
8[f]	 **(6a)**	6	97	 **(6b)**	83
9	 **(7a)**	4	>99	 **(7b)**	99
10	 **(8a)**	24	50	 **(8b)**	33
11[g]	 **(9a)**	48	94	 **(9b)**	88[h]
12[g]	 **(10a)**	48	98	 **(10b)**	51[i]

[a] Reaction conditions: substrate (0.3 mmol), $Ru(OH)_x/Al_2O_3$ (Ru: 5 mol %), water (1.5 mL), 373 K, under 1 atm of molecular oxygen. [b] Conversions were determined by ^1H NMR and/or GC analyses of the crude reaction mixture and based on the starting materials. [c] Isolated yields based on the starting materials. All isolated products were identified by ^1H and ^{13}C NMR spectroscopic analyses (Supporting Information). [d] Under 1 atm of air instead of molecular oxygen. [e] Unidentified byproducts were formed. [f] Substrate (0.2 mmol), water (1 mL). [g] 363 K. [h] Diphenol (6% select.) was formed. [i] Diphenol, C−O coupling products, and unidentified byproducts were formed.

Reaction Mechanism. According to the literature,[4−6,13] the oxidative biaryl coupling can proceed through the following three mechanisms: (i) the homolytic coupling ($A^\bullet + B^\bullet$), (ii) the heterolytic coupling ($A^+ + B$), and (iii) the radical-anion coupling ($A^\bullet + B^-$). To clarify the mechanism of the present $Ru(OH)_x/Al_2O_3$-catalyzed oxidative coupling, we attempted the competitive reaction of two substrates with different oxidation potentials (E_{ox}), **1a** (E_{ox} = 1.15 V vs SCE[14]) and 3-carbomethoxy-2-naphthol (**11a**, 1.55 V[14]). Because the E_{ox} value of **1a** is smaller than that of **11a**, the homo-coupling should lead

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(13) (a) Smŕcina, M.; Vyskŏcil, S.; Máca, B.; Polá×f0ek, M.; Claxton, T. A.; Abbott, A. P.; Kŏcovsk'y, P. *J. Org. Chem.* **1994**, *59*, 2156. (b) Hovorka, M.; Šcigel, R.; Gunterová, J.; Tich×c6, M.; Závada, J. *Tetrahedron* **1992**, *48*, 9503. (c) Hovorka, M.; Závada, J. *Tetrahedron* **1992**, *48*, 9517.

(14) The data were taken from ref 13a.

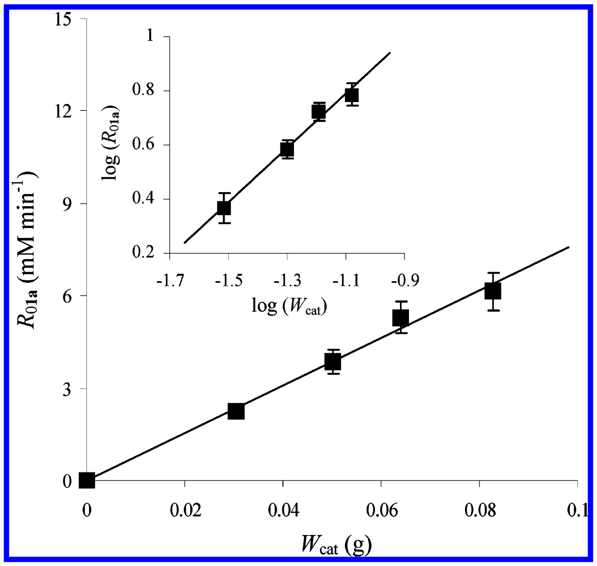


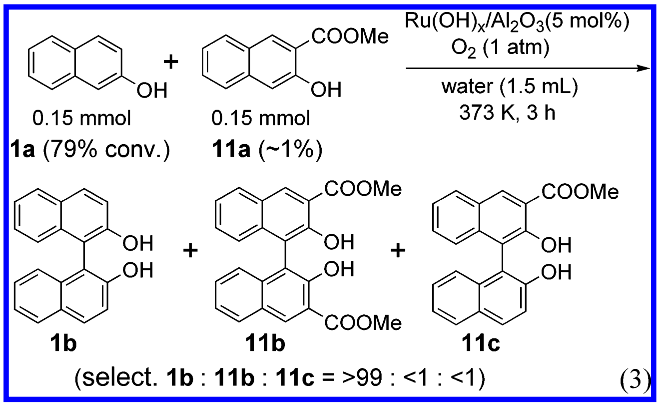
Figure 1. Dependence of the initial rate (R_{01a}) on the amount of Ru(OH)$_x$/Al$_2$O$_3$ (W_{cat}). Reaction conditions: **1a** (0.20 M), Ru(OH)$_x$/Al$_2$O$_3$ (Ru: ∼6.5 mol %), water (1.5 mL), 373 K, under 1 atm of molecular oxygen. R_{01a} values were determined by the slopes of the conversion versus time curves at low conversion (<10%) of **1a**. Slope from the inset = 1.00.

Table 3. Recycling of the Ru(OH)$_x$/Al$_2$O$_3$ Catalyst for the Oxidative Coupling of **1a**[a]

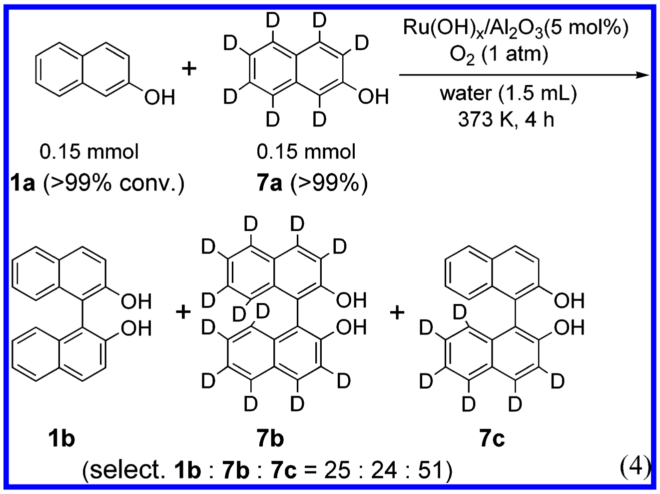
recycle no.	conv. of **1a**[b] (%)	yield of **1b**[c] (%)
fresh	>99	98
1	>99	98
2	>99	93
3	>99	97
4	>99	94
5	>99	91
6	>99	96
7	>99	93

[a] Reaction conditions: **1a** (0.3 mmol), Ru(OH)$_x$/Al$_2$O$_3$ catalyst (metal: 5 mol %), water (1.5 mL), 373 K, 4 h, under 1 atm of molecular oxygen. The reaction rates for the recycle runs were the same as that for the first run with fresh Ru(OH)$_x$/Al$_2$O$_3$ catalyst. [b] Conversions were determined by ^{1}H NMR analyses of the crude reaction mixture and based on **1a**. [c] Isolated yields based on **1a**.

to a mixture reflecting the relative reactivity and homo-coupled **1b** would predominate. In the heterolytic coupling, more easily oxidizable **1a** is oxidized to form the cationic species, which undergoes electrophilic attack to more nucleophilic **1a**. In this case, the homo-coupling product **1b** would also be a main product. If the present oxidative coupling in water proceeds via the heterolytic coupling mechanism, water and hydroxyl groups on the catalyst can act as nucleophiles, resulting in the formation of hydroxylated products.[15] However, in the present system, no hydroxylation proceeded. Therefore, we exclude the heterolytic coupling mechanism. Alternatively, the radical-anion coupling mechanism would lead to the cross-coupling product (**11c**) predominantly because the more stable anion from **11a** would attack the radical formed from more oxidizable **1a**.[16] With Ru(OH)$_x$/Al$_2$O$_3$ catalyst, the homo-coupling product of **1b** was obtained as a major product under the conditions in eq 3. This fact shows that the present oxidative biaryl coupling reaction proceeds via the homolytic coupling of two radical species.



The competitive oxidations of structurally similar 2-naphthols **1a**−**4a** under 1 atm of argon were carried out, and the respective initial rates (consumption of substrates) were expressed by R_{01a}, R_{02a}, R_{03a}, and R_{04a}. The relative reactivity decreased in the following order: **3a** (R_{03a}/R_{01a} = 1.87) > **4a** (R_{04a}/R_{01a} = 1.23) > **1a** (1.00) > **2a** (R_{02a}/R_{01a} = 0.72). As shown in Figure 2, the reactivity for **1a**−**4a** increased with an increase in the HOMO orbital energies. Because the E_{ox} values increase with a decrease in the HOMO orbital energies of neutral molecules of the parent molecules such as **1a** and **11a**,[13a] the good correlation between log(R_0/R_{01a}) and the HOMO orbital energy shows that the reaction rates increased with a decrease in E_{ox} values, supporting the radical−radical homolytic coupling mechanism. In the competitive oxidation of **1a** and **7a** with the same oxidation potential, **1b**, **7b**, and the cross-coupling product **7c** were obtained in 25%, 24%, and 51% selectivities (1:1:2 ratio), respectively, at quantitative conversion of **1a** and **7a** (eq 4). These selectivities were almost unchanged in the conversion range of 0−99%. These results also support the present reaction mechanism.



The reaction of **1a** was carried out at 373 K under 1 atm of argon, and the Ru(OH)$_x$/Al$_2$O$_3$ was recovered under argon. The ESR spectrum of the recovered catalyst was then measured at 290 K under argon. As shown in Figure 3a, a sharp signal at g = 2.0044 was observed. The signal is possibly assignable to a radical species derived from **1a**, for example, a naphthoxy radical. The signal was not observed after the treatment of Ru(OH)$_x$/Al$_2$O$_3$ without **1a**. The Ru(OH)$_x$/Al$_2$O$_3$ catalyst re-

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(15) (a) Yamaguchi, K.; Matsushita, M.; Mizuno, N. *Angew. Chem., Int. Ed.* **2004**, *43*, 1576. (b) Kamata, K.; Kasai, J.; Yamaguchi, K.; Mizuno, N. *Org. Lett.* **2004**, *6*, 3577.

(16) For the anion-radical coupling mechanism, more easily reducible **11a** is reduced to form the anionic species, while the radical from **1a** prefers to act as an electrophilic radical. Therefore, the radical from **1a** preferably interacts with the anion from **11a** rather than that from **1a**, giving the cross-coupling products predominantly. See ref 13a.

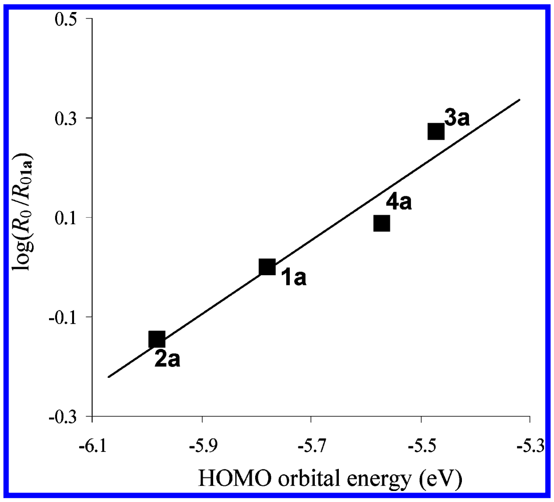


Figure 2. Relative initial rates for the competitive oxidative coupling of **1a**−**4a** as a function of the HOMO orbital energies. Reaction conditions: **1a** (0.15 mmol) + **2a**, **3a**, or **4a** (0.15 mmol), $Ru(OH)_x/Al_2O_3$ (Ru: 5 mol %), water (1.5 mL), 353 K, under 1 atm of argon. The initial rates were determined by the slopes of the conversion versus time curves below 5% conversions of the substrates.

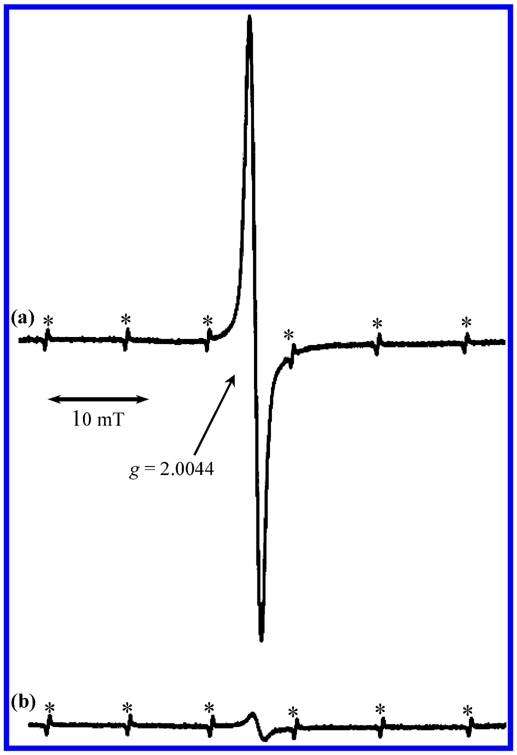


Figure 3. ESR spectra of $Ru(OH)_x/Al_2O_3$ measured at 290 K under argon. (a) $Ru(OH)_x/Al_2O_3$ (5 mol %) was treated with **1a** (0.3 mmol) in water under 1 atm of argon at 373 K. After 4 h, the catalyst was recovered and the spectrum was measured. (b) The recovered catalyst (a) was treated with phenyl *N*-*tert*-butylnitron at room temperature for 1 h. Asterisks were assigned to the signals of the Mn marker.

covered was successively treated with phenyl *N*-*tert*-butylnitron (0.1 M) in toluene at room temperature for 1 h under 1 atm of argon. After the treatment, the catalyst was recovered by the filtration under argon and the ESR spectrum of the catalyst was again measured. The signal almost disappeared with the treatment using phenyl *N*-*tert*-butylnitron (Figure 3b). The ESR spectrum of the filtrate was also measured at 178 K under argon. As shown in Figure 4, a very sharp triplet signal was observed and the spectrum was well reproduced by the simulation with the following parameters: $g = 2.0067$, $A_N = 1.54$, $A_H = 0.11$ mT. The signal intensity of Figure 4 corresponded to the 0.2 mol % nitroxide spin adducts with respect to the amount of ruthenium species loaded. According to the literature,[17] this signal is assignable to the nitroxide spin adduct formed by the reaction of phenyl *N*-*tert*-butylnitron with the radical species. The ESR results indicate that the radical species is formed on the surface of $Ru(OH)_x/Al_2O_3$ (intermediate **A** in Scheme 1).

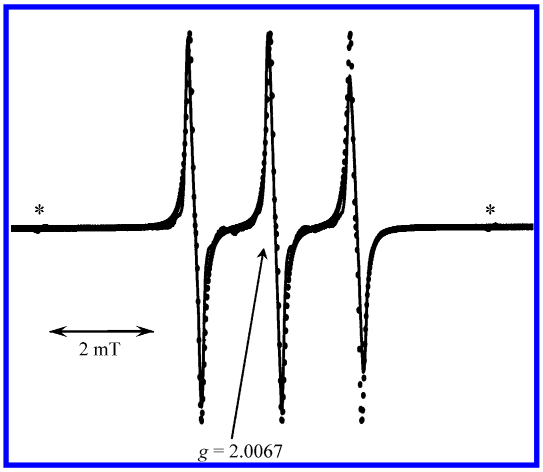
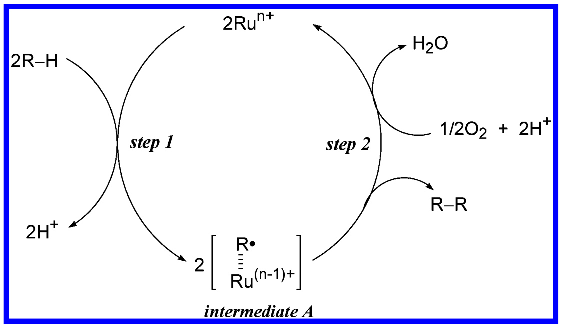


Figure 4. A ESR spectrum of the nitroxide spin adduct obtained by the treatment of phenyl *N*-*tert*-butylnitron with the $Ru(OH)_x/Al_2O_3$ recovered after the reaction with **1a** under argon. $Ru(OH)_x/Al_2O_3$ (5 mol %) was reacted with **1a** (0.3 mmol) in water under 1 atm of argon at 373 K. After 4 h, the catalyst was recovered and treated with phenyl *N*-*tert*-butylnitron (0.1 M) in toluene at room temperature for 1 h. After the treatment, the catalyst was recovered and the ESR spectrum of the filtrate was measured at 178 K under argon. The dotted line was obtained by the simulation (see text). Asterisks were assigned to the signals of the Mn marker.

Scheme 1



The XPS measurements showed that the Ru $3p_{3/2}$ and $3d_{5/2}$ binding energies of the fresh $Ru(OH)_x/Al_2O_3$ was detected at 463.5 eV (full width at the half-maximum (fwhm) 4.7 eV) and 281.8 eV (fwhm 2.4 eV), respectively, indicating that the oxidation state of ruthenium species on $Ru(OH)_x/Al_2O_3$ is +3.[18] The Ru $3p_{3/2}$ and $3d_{5/2}$ binding energies of the catalyst recovered after the reaction with **1a** under argon were detected at 462.9 eV (fwhm 4.5 eV) and 281.4 eV (fwhm 2.6 eV), respectively, and were by 0.6 and 0.4 eV lower than those of the fresh one, respectively. These results suggest that the average oxidation state of the ruthenium species of the recovered catalyst is lower

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(17) Church, D. F. *Anal. Chem.* **1994**, *66*, 419.

(18) (a) Mitchell, P. C. H.; Scott, C. E.; Bonnelle, J. P.; Grimblot, J. G. *J. Catal.* **1987**, *107*, 482. (b) Nagai, M.; Koizumi, K.; Omi, S. *Catal. Today* **1997**, *35*, 393. (c) Murata, S.; Aika, K. *J. Catal.* **1992**, *136*, 110. (d) Aika, K.; Ohya, A.; Ozaki, A.; Inoue, Y.; Yasumori, I. *J. Catal.* **1985**, *92*, 305. (e) Williams, G. P. In *CRC Handbook of Chemistry and Physics*, 82nd ed.; Lida, D. R., Ed.; CRC Press: Washington, DC, 2001; Section 10, pp 200−205.

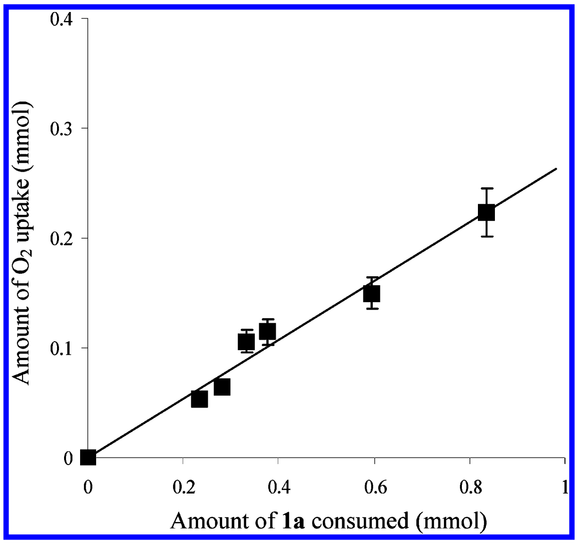

Figure 5. Relationship between the amounts of **1a** consumed and O_2 uptake for the oxidative coupling of **1a** with molecular oxygen by $Ru(OH)_x/Al_2O_3$. Reaction conditions: **1a** (0.6−1.0 mmol), $Ru(OH)_x/Al_2O_3$ (Ru: 5 mol %), water (3 mL), 373 K, under 1 atm of molecular oxygen. Slope (O_2 uptake/**1a** consumed) = 0.27.

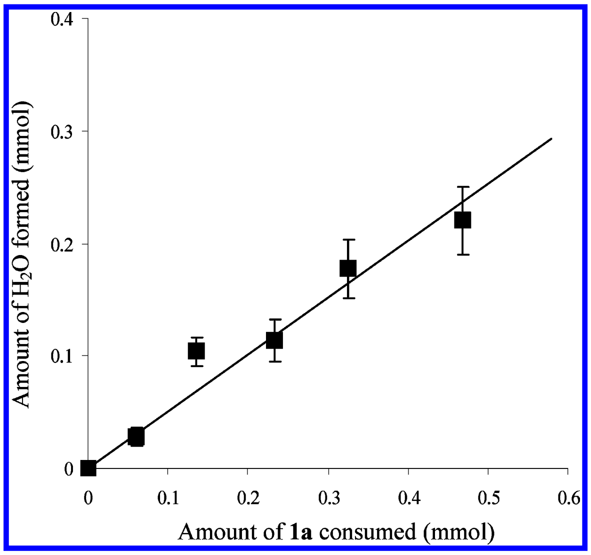

Figure 6. Relationship between the amounts of **1a** consumed and H_2O formed for the oxidative coupling of **1a** with molecular oxygen by $Ru(OH)_x/Al_2O_3$. Prior to the reaction, $Ru(OH)_x/Al_2O_3$ was treated with D_2O at 373 K for 1 h. After the treatment, H_2O from $Ru(OH)_x/Al_2O_3$ can be negligible. The reaction was carried out in D_2O, and the amount of H_2O (and HDO) formation was determined by ^1H NMR. Two moles of HDO were regarded as one mole of H_2O. Reaction conditions: **1a** (0.06−0.45 mmol), $Ru(OH)_x/Al_2O_3$ (Ru: 15 μmol), D_2O (1.5 mL), 363 K, under 1 atm of molecular oxygen. Slope (water formed/**1a** consumed) = 0.51.

than that (+3) on the fresh $Ru(OH)_x/Al_2O_3$. Because the binding energies of Ru $3p_{3/2}$ and $3d_{5/2}$ of Ru(0) have been reported to be 461.5 and 280.0 eV, respectively,[18] the oxidation state of ruthenium species of the recovered catalyst is not zero. The lower oxidation state of the ruthenium species of the recovered catalyst is possibly assigned to Ru^{2+}, which is formed by the one-electron transfer from **1a**.

The measurements of O_2 uptake and H_2O formation during the oxidative coupling of **1a** were carried out. As shown in Figures 5 and 6, the amounts of O_2 uptake and H_2O formation were almost one-quarter and one-half of the amount of **1a** consumed, respectively. Under the anaerobic conditions, the amount of **1b** formed was approximately one-half the amount of ruthenium loaded.

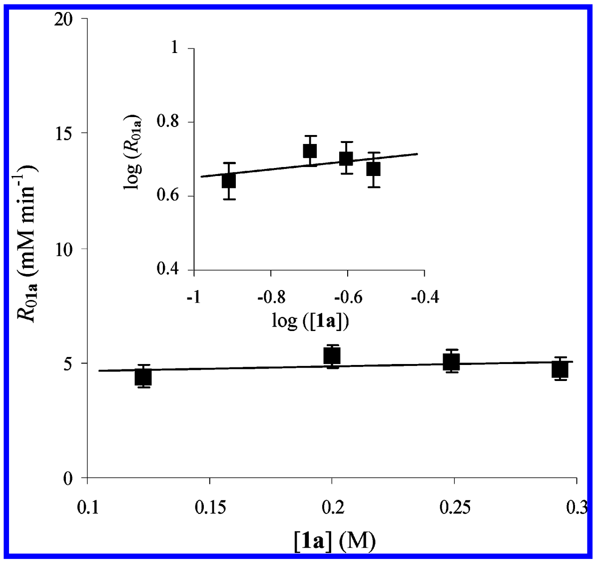

Figure 7. Dependence of the initial rate (R_{01a}) on the concentration of **1a** ([**1a**]). Reaction conditions: **1a** (0.12−0.29 M), $Ru(OH)_x/Al_2O_3$ (Ru: 5 mol %), water (1.5 mL), 373 K, P_{O_2} = 1.0 atm. R_{01a} values were determined by the slopes of the conversion versus time curves at low conversion (<10%) of **1a**. Slope from the inset = 0.11.

On the basis of the above experimental results, we here propose the possible reaction mechanism for the present oxidative coupling reaction (Scheme 1). This reaction can be divided into two steps. The reaction proceeds with a typical radical mechanism via the one-electron transfer from a substrate to $Ru(OH)_x/Al_2O_3$ to give the reduced form and a radical species (intermediate **A**) (step 1 in Scheme 1). Two radical species are then coupled to give the corresponding biaryl coupling product, and the reduced catalyst reacts with molecular oxygen to regenerate the oxidized form with the formation of water (step 2 in Scheme 1).

As mentioned, Al_2O_3 showed no catalytic activity for the present oxidative coupling reaction. Therefore, the one-electron oxidation probably occurs on the ruthenium species. Among the ruthenium species supported on various metal oxides, $Ru(OH)_x/Al_2O_3$ was found to be the most active catalyst, and the order of catalytic activity decreased as follows: $Ru(OH)_x/Al_2O_3$ > $Ru(OH)_x/TiO_2$ > $Ru(OH)_x/SiO_2$ (entries 1, 7, and 8 in Table 1). This order is in good accord with that of their basicities,[19] indicating that the basic sites of the catalysts also play a role in the present oxidative coupling reaction. The proton abstraction from the substrate or cation radical species would occur during the reaction (step 1 in Scheme 1), which is promoted by the basic sites of the catalysts.

The reaction rate for the oxidative coupling of **1a** was almost independent of the concentration of **1a** (0.12−0.29 M, Figure 7), while the first-order dependence of the reaction rate on the partial pressure of molecular oxygen (0.2−1.0 atm, Figure 8) was observed. A kinetic isotope effect (k_H/k_D) of 1.0 (±0.1) was observed for the oxidative coupling of 2-naphthol (**1a**) and 2-naphthol-1,3,4,5,6,7,8-d_7 (**7a**) at 373 K, showing that the C−H bond cleavage is not included in the rate-limiting step. Kinetic

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(19) The basicities of the catalysts (the equilibrium amount of acetic acid adsorption, see Experimental Section) decreased in the order of $Ru(OH)_x/Al_2O_3$ (0.71 mmol g^{-1}) > $Ru(OH)_x/TiO_2$ (0.46 mmol g^{-1}) > $Ru(OH)_x/SiO_2$ (0.23 mmol g^{-1}).

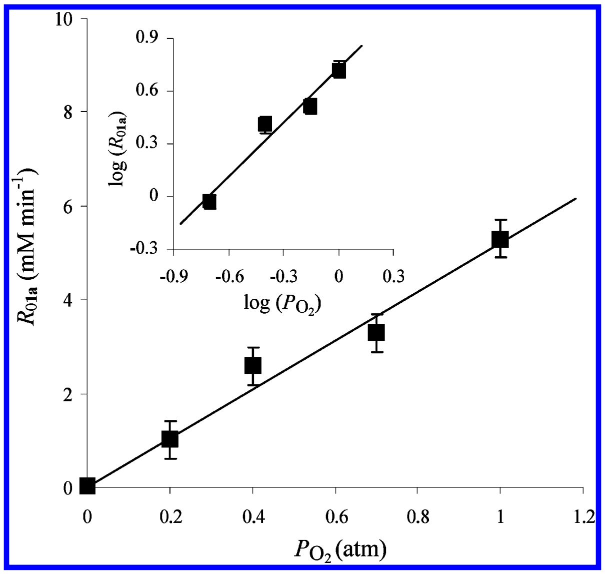

Figure 8. Dependence of the initial rate (R_{01a}) on the partial pressure of molecular oxygen (P_{O_2}). Reaction conditions: **1a** (0.20 M), Ru(OH)$_x$/Al$_2$O$_3$ (Ru: 5 mol %), water (1.5 mL), 373 K, P_{O_2} = 0.2−1.0 atm. R_{01a} values were determined by the slopes of the conversion versus time curves at low conversion (<10%) of **1a**. Slope from the inset = 1.01.

data and kinetic isotope effect show that the radical formation smoothly proceeds (step 1 in Scheme 1) and that the reoxidation is the rate-limiting step (step 2 in Scheme 1). The reaction rate of stoichiometric oxidation of **1a** (under 1 atm of argon at 353 K) was 4.3 mM min^{-1} and faster than that of catalytic oxidation under the same reaction conditions, consistent with the idea that step 2 is the rate-limiting step.

Conclusion

We can develop the efficient aerobic oxidative biaryl coupling system with Ru(OH)$_x$/Al$_2$O$_3$ catalyst. From the standpoint of “green chemistry and technology”, the present system has the following significant advantages: (i) the use of molecular oxygen as a sole oxidant, (ii) the use of water as a solvent, (iii) the applicability to various 2-naphthols and substituted phenols, (iv) the high turnover number, (v) simple workup procedures, for example, catalyst/product separation, (vi) reusability of Ru(OH)$_x$/Al$_2$O$_3$, and (vii) the use of easily prepared and inexpensive Ru(OH)$_x$/Al$_2$O$_3$ catalyst. The mechanistic and kinetic investigations show that the Ru(OH)$_x$/Al$_2$O$_3$-catalyzed aerobic oxidative biaryl coupling reaction proceeds through the radical−radical coupling mechanism. The catalyst acts as a one-electron oxidant to form the reduced form and a radical species. The reduced catalyst is reoxidized by molecular oxygen. The latter step is included in the rate-limiting step.

Experimental Section

General. NMR spectra were recorded on a JEOL JNM-EX-270 spectrometer. ^{1}H and ^{13}C NMR spectra were measured at 270 and 67.5 MHz, respectively, in CDCl$_3$ or CD$_3$CN with TMS as an internal standard. GC analyses were performed on a Shimadzu GC-14B with a flame ionization detector equipped with a TC-1 capillary column (internal diameter = 0.25 mm, length = 30 m). Mass spectra were recorded on a Shimadzu GCMS-QP2010 at an ionization voltage of 70 eV equipped with a DB-WAX capillary column (internal diameter = 0.25 mm, length = 30 m). ESR measurements at 290 K (X-band) were performed with a JEOL JES-RE-1X spectrometer. XPS measurements were carried out on JEOL JPS-90 using monochromated Al Kα radiation ($h\nu$ = 1486.6 eV). The X-ray anode was run at 200 W, and the voltage was kept at 10 kV. The pass energy was fixed at 20.0 eV to ensure sufficient resolution to accurately determine peak positions. The binding energies were calibrated by using Al 2p signal at 74.8 eV. 2-Naphthols and substituted phenols were commercially obtained from Tokyo Kasei, Aldrich, and Fluka (reagent grade) and were used without further purification. 2-Naphthol-1,3,4,5,6,7,8-d_7 (99.5% purity, 97.5 at. % D) was obtained from ISOTEC and used without further purification. Alumina (KHS-24, BET surface area: 160 m^2 g^{-1}) was supplied from Sumitomo Chemical Co., Ltd. All products (**1b**−**10b**) have been identified by comparison of their ^{1}H and ^{13}C NMR signals with the literature data (see Supporting Information).[4−6]

Preparation of Ru(OH)$_x$/Al$_2$O$_3$ Catalyst. The Ru(OH)$_x$/Al$_2$O$_3$ catalyst was prepared according to the procedure reported previously.[20] The powder Al$_2$O$_3$ (2.0 g) calcined at 823 K for 3 h was vigorously stirred with 60 mL of an aqueous solution of RuCl$_3$ (8.3 mM) at room temperature. After 15 min, the pH of the solution was slowly adjusted to 13.2 by addition of an aqueous solution of NaOH (1.0 M), and the resulting slurry was stirred for 24 h. The solid was then filtered off, washed with a large amount of water, and dried in vacuo to afford 2.1 g of Ru(OH)$_x$/Al$_2$O$_3$ as a dark green powder. The content of ruthenium was 2.0−2.1 wt %. The content of ruthenium is controllable by changing the concentration of the starting ruthenium solution. The XRD pattern of Ru(OH)$_x$/Al$_2$O$_3$ was the same as that of the parent Al$_2$O$_3$ support, and no signal due to Ru metal (clusters) and RuO$_2$ was observed. Particles of Ru metal (clusters) and RuO$_2$ were not detected by TEM micrograph. XPS shows that binding energies of Ru 3d$_{5/2}$ and Ru 3p$_{3/2}$ of Ru(OH)$_x$/Al$_2$O$_3$ were detected at 281.8 eV (full width at the half-maximum, fwhm 2.4 eV) and 463.5 eV (fwhm 4.7 eV), respectively, showing that the oxidation state of ruthenium species on Ru(OH)$_x$/Al$_2$O$_3$ is +3.[18] The IR spectrum showed a very broad ν(OH) band in the range of 3000−3700 cm^{-1}. These facts suggest that ruthenium(III) hydroxide is highly dispersed on Al$_2$O$_3$. Other transition metal hydroxide supported on Al$_2$O$_3$ catalysts, M(OH)$_x$/Al$_2$O$_3$ (M = Pd, Rh, Pt, V, Fe, and Cu) and ruthenium hydroxide on SiO$_2$ and TiO$_2$ were prepared by a procedure similar to that for Ru(OH)$_x$/Al$_2$O$_3$.

A Typical Procedure for the Oxidative Biaryl Coupling. Into a Pyrex-glass vial were successively placed Ru(OH)$_x$/Al$_2$O$_3$ (Ru: 5 mol %), 2-naphthol (1.08 g, 7.5 mmol), and water (37.5 mL). A Teflon-coated magnetic stir bar was added, and the reaction mixture was vigorously stirred (800 rpm) at 373 K under 1 atm of molecular oxygen (equipped with a balloon). After 4 h, the catalyst and the product were separated by filtration, and the solid mixture was washed with a large amount of acetonitrile. Acetonitrile solution of the crude product was then evaporated in vacuo, and the crude product was purified by recrystallization from benzene to give analytically pure pale-yellow crystals of BINOL (1.04 g, 97% isolated yield). The separated Ru(OH)$_x$/Al$_2$O$_3$ was washed with an aqueous solution of NaOH (pH = 13.2) and water, and then dried in vacuo before recycling.

Measurements of Acetic Acid Adsorption. The measurements of the amount of acetic acid adsorption were carried out in water. A typical procedure was as follows: The finely ground catalyst (Ru(OH)$_x$/Al$_2$O$_3$, Ru(OH)$_x$/TiO$_2$, or Ru(OH)$_x$/SiO$_2$, 0.10 g) was placed in a Pylex-glass vial with a Teflon-coated magnetic stir bar, and 1.0 mL of D$_2$O solution of acetic acid (0.36 M) was added. The operations were carried out under 1 atm of argon at 300 K. The amounts of acetic acid adsorbed on the catalyst were evaluated by the decreases in the acetic acid concentrations in the liquid phase, which were determined by GC and ^{1}H NMR analyses. The equilibrium of acetic acid adsorption on the catalyst was reached within ca. 10 min in each case. The equilibrium amount of acetic acid adsorption was regarded as a measure of the basicity of the catalyst.

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The Calculation of HOMO Orbital Energies. The calculations were carried out with the program package Gaussian 98.[21] The HOMO orbital energies of **1a**−**4a** were calculated at the B3LYP level with 6-311G(d, p) (C, H, O) and the triple-ζ level basis sets with the efficient core potential proposed by Stevens, Basch, and Krauss (Br).[22] The order of HOMO orbital energies was **3a** (−5.47 eV) > **4a** (−5.57 eV) > **1a** (−5.78 eV) > **2a** (−5.98 eV).

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Supporting Information Available: Detailed presentation of physical data of **1b**−**10b**, Figures S1−S3. This material is available free of charge via the Internet at http://pubs.acs.org.

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