A Supported Rhodium Hydroxide Catalyst: Preparation, Characterization, and Scope of the Synthesis of Primary Amides from Aldoximes or Aldehydes

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Dedicated to Professor Ryoji Noyori on the occasion of his 70th birthday

Abstract: A supported rhodium hydroxide catalyst, $Rh(OH)_x/Al_2O_3$ ($x = 3$), is prepared by the reaction of Al_2O_3 with $RhCl_3$ in an aqueous medium followed by treatment with NaOH. The Rh^{III} hydroxide species is monomerically (or highly) dispersed on the Al_2O_3 support. $Rh(OH)_x/Al_2O_3$ acts as a reusable heterogeneous catalyst in water, rather than in an explosive, hazardous, and carcinogenic organic solvent, for the synthesis of primary amides from aldoximes or aldehydes by an efficient sequential process of dehydration and rehydration. The dehydrative condensation of aldehydes and hydroxylamine is also promoted by the $Rh(OH)_x/Al_2O_3$ catalyst.

Keywords: aldehydes · aldoximes · heterogeneous catalysis · primary amides · rhodium hydroxide

Introduction

Amides are an important class of chemicals that have widely been used as chemical intermediates in organic synthesis, raw materials for engineering plastics, detergents, and lubricants.[1] The rearrangement of oximes is a good candidate for the amide synthesis because its atom efficiency is theoretically 100%. Although *N*-substituted amides can generally be obtained in high yields by the acid-catalyzed rearrangement of ketoximes (Beckmann rearrangement),[2,3] the reaction of aldoximes gives the corresponding nitriles rather than primary amides in the presence of acid catalysts. The synthesis of primary amides from aldoximes is very difficult and reactive reagents have been used in stoichiometric amounts for the transformation.[4,5] Aldoximes are generally synthesized by the dehydrative condensation of the corresponding aldehydes with hydroxylamine (an excess amount with respect to aldehydes) in organic solvents in the presence of a base such as pyridine.[6] Thus, if the synthesis of primary amides directly from aldehydes and hydroxylamine could be performed, it would be more economical and environmentally-friendly. However, stoichiometric reagents such as CH_3SO_3H, CH_3SO_2Cl, and ZnO have been used for the direct synthesis with an excess amount of hydroxylamine.[7,8] Therefore, the development of efficient catalytic procedures for the synthesis of primary amides from aldoximes or aldehydes is a great challenge. The heterogeneous catalytic transformations in either water or completely without a solvent are environmentally and technologically the most desirable procedures.[9,10]

Our strategy to design the efficient heterogeneous catalysts for various functional group transformations is a creation of the monomerically (or highly) dispersed metal hydroxide species on the appropriate supports.[11] The metal hydroxide species possess both Lewis acid and Brønsted base sites on the same metals, and the various functional group transformations are likely promoted by the "concerted activation" of the Lewis acid and Brønsted base sites.[11] For example, it has been reported that the mechanism for the nitrile hydration by monomeric Co^{III}–OH complexes involves coordination of a nitrile to the Co^{III} center, and that the intramolecular nucleophilic attack of the hydroxide species on the proximal activated nitrile carbon proceeds easily.[12] This concerted activation of the Lewis acid (Co^{III} center) and Brønsted base (hydroxide species) sites provid-

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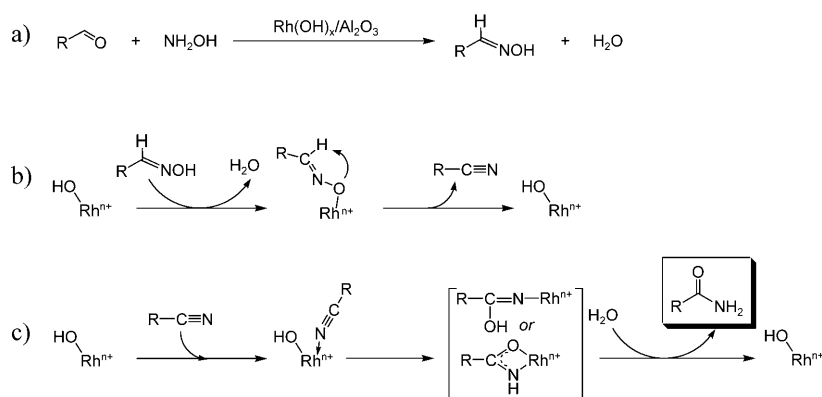
Scheme 1. A possible reaction mechanism for the transformation of aldoximes or aldehydes to the corresponding amides.

ed over a 10^{10}-fold rate acceleration for the hydration of acetonitrile.[12]

The transformations of aldoximes or aldehydes to the corresponding primary amides are likely promoted by the concerted activation using the dehydration–rehydration sequence (Scheme 1). Thus, various kinds of supported metal hydroxide catalysts have been prepared and used for the transformation of benzaldoxime (**1a**) to benzamide. It was found that the supported platinum group metal hydroxides, especially the supported rhodium hydroxide $Rh(OH)_x/Al_2O_3$, showed high catalytic activity and selectivity for the transformation (Figure 1).[11f] In this paper, we report the preparation and characterization of the supported rhodium
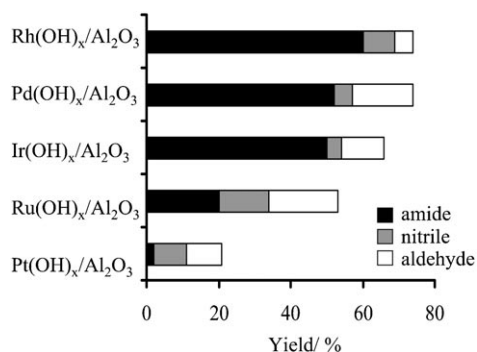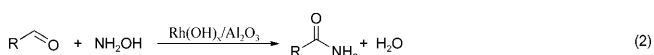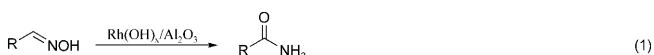

Figure 1. The transformation of benzaldoxime (**1a**) by various platinum group metal hydroxide catalysts. Reaction conditions: **1a** (0.5 mmol), catalyst (metal: 4 mol %), water (2 mL), 160 °C, 4 h.

hydroxide catalyst $Rh(OH)_x/Al_2O_3$, the scope of the $Rh(OH)_x/Al_2O_3$-catalyzed transformations of aldoximes and aldehydes [Eq. (1) and (2)], and full details of the reaction mechanism.

Results and Discussion

Preparation and Characterization of the Supported Rhodium Hydroxide Catalyst $Rh(OH)_x/Al_2O_3$

The $Rh(OH)_x/Al_2O_3$ catalyst was prepared by the reaction of Al_2O_3 with $RhCl_3$ in an aqueous medium followed by treatment with NaOH. The powder Al_2O_3 (2.0 g) calcined at 823 K for 3 h was vigorously stirred with an aqueous solution of $RhCl_3$ (60 mL, 6.5 mM) at room temperature. After 15 min, the pH of the solution was quickly adjusted to 13.2 with an aqueous solution of NaOH (1.0 M), and the slurry was stirred for 24 h at room temperature. The resulting yellow powder was then filtered off, washed with a large amount of deionized water, and dried in vacuo to afford the $Rh(OH)_x/Al_2O_3$ (2.0 g, 2.1 wt % rhodium content) catalyst. The BET surface area of $Rh(OH)_x/Al_2O_3$ was 172 $m^2 g^{-1}$ and was close to that of the parent Al_2O_3 (174 $m^2 g^{-1}$). The IR spectrum of $Rh(OH)_x/Al_2O_3$ showed a broad $\nu(OH)$ band in the range of 3000–3770 cm^{-1}. The XRD pattern of $Rh(OH)_x/Al_2O_3$ was the same as that of the parent Al_2O_3 support and no signals arising from rhodium metal (clusters) and rhodium oxides were observed.[13] The $Rh(OH)_x/Al_2O_3$ catalyst was completely ESR silent. The X-ray photoelectron spectroscopy (XPS) spectrum of $Rh(OH)_x/Al_2O_3$ showed the binding energies of Rh $3d_{5/2}$ and Rh $3d_{3/2}$ at 310.0 (full width at the half maximum, FWHM 1.4 eV) and 314.8 eV (FWHM 1.4 eV), respectively, suggesting that the oxidation state of rhodium species is +3 ($x = 3$).[14] Furthermore, no chlorine was detected in the $Rh(OH)_x/Al_2O_3$ catalyst.

Figure 2 shows the radial distribution functions from the Fourier transform of the k^3-weighed extended X-ray absorption fine structure (EXAFS) for $Rh(OH)_x/Al_2O_3$ and anhydrous Rh_2O_3 with corundum structure. The first Rh−O shell parameters for $Rh(OH)_x/Al_2O_3$ are similar to those for anhydrous Rh_2O_3.[15] In contrast to anhydrous Rh_2O_3, the signals arising from the Rh−O−Rh shells at $R = 2.6$ and 3.4 Å are hardly observed for the radial distribution function of $Rh(OH)_x/Al_2O_3$. The absence of the Rh−O−Rh shell signals suggests that no networks of linked RhO_6 octahedrals exist in $Rh(OH)_x/Al_2O_3$. All these results suggest that Rh^{III} hydroxide is monomerically (at least mainly if not wholly) dispersed on Al_2O_3.

Scope of the $Rh(OH)_x/Al_2O_3$-Catalyzed Synthesis of Primary Amides from Aldoximes or Aldehydes

By using the $Rh(OH)_x/Al_2O_3$ catalyst,[16] various kinds of structurally diverse aldoximes including aromatic, aliphatic, unsaturated, and heterocyclic, can be converted into the cor-
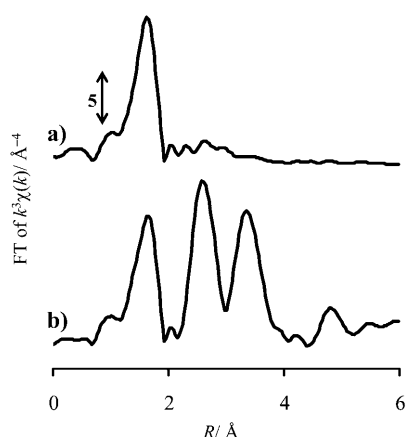
Figure 2. The radial distribution functions from the Fourier transform (FT) of the k^3-weighed EXAFS for a) $Rh(OH)_x/Al_2O_3$ and b) anhydrous Rh_2O_3. The phase shift was not corrected.

responding primary amides in high to excellent yields in water under conditions entirely free of explosive, hazardous, and carcinogenic organic solvents. The results are summarized in Table 1. In contrast to the transformations in water, nitriles were formed as major products in common organic solvents [Eq. (3)]. Under the conditions described in Table 1, no amides were produced in the absence of the catalyst, or in the presence of Al_2O_3 or anhydrous Rh_2O_3. In the case of the catalyst precursor of homogeneous

$RhCl_3\cdot 3H_2O$, the selectivities to the corresponding amides were low, especially for aliphatic aldoximes. For example, n-dodecanaldoxime was completely consumed under the conditions described in Table 1 and the corresponding amide was obtained in 68% yield along with the formation of carboxylic acid (12%), nitrile (3%), and unidentified by-products.
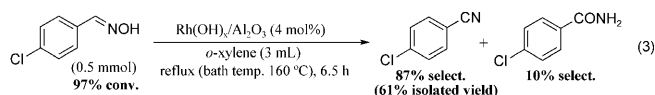
The $Rh(OH)_x/Al_2O_3$-catalyzed transformations of benzaldoximes (**1a**–**7a**), which contain electron-donating as well as electron-withdrawing substituents, proceed readily to give the corresponding benzamides (Table 1, entries 1–8). In the transformations of methoxybenzaldoximes, the lower reaction rate of o-methoxybenzaldoxime (**2a**) relative to p-methoxybenzaldoxime (**3a**) indicates a steric effect (Table 1, entry 3 vs. 4). This observation suggests that the substrates coordinate to the metal center on the surface of $Rh(OH)_x/Al_2O_3$, and the transformation proceeds through intramolecular attack of the rhodium hydroxide species on the coordinated substrates. A similar steric effect was observed for the $Ru(OH)_x/Al_2O_3$-catalyzed hydration of nitriles.[11d]

Also, nonactivated aliphatic aldoximes, including linear (**8a** and **11a**), branched (**9a** and **10a**), and cyclic (**12a**) forms, are converted to the corresponding aliphatic amides in high yields (Table 1, entries 9–14). The reaction of unsaturated aldoximes (**13a** and **14a**) efficiently proceeds to afford the corresponding unsaturated amides without the geometrical isomerization and hydration of the double bonds (Table 1, entries 15 and 16). The reaction of heterocyclic aldoximes, including oxygen (**15a**) and sulfur (**16a**) in the substrates, did not alter the conversion and selectivity, and the corresponding heterocyclic amides were obtained in high yields (Table 1, entries 17 and 18). Moreover, the $Rh(OH)_x/Al_2O_3$ catalyst can be reused without a significant loss of the catalytic activity (Table 1, entries 2 and 13).

Interestingly, the $Rh(OH)_x/Al_2O_3$ catalyst can be applied to the tandem one-pot synthesis of primary amides from the corre-

Table 1. The $Rh(OH)_x/Al_2O_3$-catalyzed synthesis of amides from aldoximes.[a]

Entry	Substrate[b]	Temp. [°C]	Time [h]	Conv. of oxime [%]	Selectivity [%] Amide[c]	Nitrile	Aldehyde	Acid
1	**1a** ($E > 95\%$)	160	7	> 99	85(76)	8	7	< 1
2[d]	**1a** ($E > 95\%$)	160	7	94	81	8	11	< 1
3	**2a** ($E > 95\%$)	160	7	67	75	15	10	< 1
4	**3a** ($E > 95\%$)	160	7	> 99	85(88)	5	10	< 1
5	**4a** ($E > 95\%$)	160	7	> 99	97(77)	1	2	< 1
6	**5a** ($E > 95\%$)	160	7	> 99	95(87)	1	4	< 1
7	**6a** ($E > 95\%$)	160	7	> 99	92(90)	< 1	8	< 1
8	**7a** ($E > 95\%$)	160	7	> 99	76(63)	7	17	< 1
9	**8a** ($E/Z = 59/41$)	140	7	> 99	98(83)	1	< 1	< 1
10	**9a** ($E/Z = 67/33$)	140	7	> 99	96(86)	4	< 1	< 1
11	**10a** ($E/Z = 55/45$)	140	7	> 99	99(86)	< 1	1	< 1
12	**11a** ($E/Z = 54/46$)	140	7	> 99	93(84)	5	< 1	2
13[d]	**11a** ($E/Z = 54/46$)	140	7	> 99	91	7	1	1
14	**12a** ($E/Z = 72/28$)	140	7	87	88(63)	8	4	< 1
15	**13a** ($E/Z = 60/40$)	160	7	> 99	92(70)	6	2	< 1
16	**14a** ($E/Z = 64/36$)	140	7	96	97(92)	3	< 1	< 1
17	**15a** ($E/Z = 36/64$)	160	7	93	98(71)	1	1	< 1
18	**16a** ($E > 95\%$)	160	7	> 99	96(84)	4	< 1	< 1

[a] Reaction conditions: Aldoxime (0.5 mmol), $Rh(OH)_x/Al_2O_3$ (Rh: 4 mol%), water (2 mL). Conversion and selectivity were determined by GC analyses. [b] Values in the parentheses are the isomer ratios of aldoximes. [c] Values in the parentheses are the yields of isolated products. [d] Reuse experiment.

sponding aldehydes and hydroxylamine.[6] Although the tandem one-pot synthesis of amides is very useful, it requires stoichiometric reagents such as CH_3SO_3H (>30 equiv with respect to aldehydes), CH_3SO_2Cl (>1 equivalent), and ZnO (>2 equiv) for the transformation with an excess amount of hydroxylamine (>3 equiv). In contrast to these stoichiometric systems, various kinds of structurally diverse aldehydes can be catalytically converted, using the $Rh(OH)_x/Al_2O_3$ catalyst, into the corresponding primary amides in high yields using only one equivalent of hydroxylamine with respect to aldehydes as summarized in Table 2.[17] The catalytic transformation of benzaldehydes

Table 2. The $Rh(OH)_x/Al_2O_3$-catalyzed one-pot synthesis of amides from aldehydes and hydroxylamine.[a]

| Entry | Substrate | Temp. [°C] | Time [h] | Conv. of aldehyde [%] | Selectivity [%] | | | |
					Amide[b]	Nitrile	Oxime	Acid
1	1b	160	7	98	86(90)	5	<1	9
2	2b	160	7	92	89(82)	2	<1	9
3	3b	160	7	98	94(85)	2	<1	4
4	4b	160	7	>99	95(84)	<1	<1	5
5	5b	120	7	>99	91(81)	2	2	5
6	6b	120	9	>99	89(89)	5	<1	6
7[c]	6b	120	9	>99	79	8	<1	13
8	7b	120	7	99	82(77)	1	<1	17
9	8b	160	7	99	88(73)	9	<1	3
10	9b	140	7	98	71(70)	3	<1	26
11	10b	160	7	>99	96(82)	1	<1	3
12	11b	160	7	99	99(85)	1	<1	<1
13	12b	160	7	85	86(81)	<1	<1	14

[a] Reaction conditions: Aldehyde (0.5 mmol), $(NH_2OH)_2 \cdot H_2SO_4$ (0.25 mmol, one equivalent with respect to an aldehyde), $Rh(OH)_x/Al_2O_3$ (Rh: 4 mol%), water (2 mL). Conversion and selectivity were determined by GC analyses. [b] Values in the parentheses are the yields of isolated products. [c] Reuse experiment.

(1b–4b) proceeds readily to afford the corresponding benzamides (Table 2, entries 1–4). The aliphatic aldehydes (5b–7b) are also converted into the corresponding aliphatic amides in high yields (Table 2, entries 5–8). The reaction of unsaturated aldehydes (8b and 9b) efficiently proceeds to afford the corresponding unsaturated amides without the geometrical isomerization and hydration of the double bonds (Table 2, entries 9 and 10). The present system was effective for heteroatom-containing aldehydes 10b–12b (Table 2, entries 11–13). Furthermore, the $Rh(OH)_x/Al_2O_3$ catalyst can be reused without a significant loss of the catalytic activity (Table 2, entry 7).

Heterogeneous Catalysis

The use of heterogeneous catalysts can make the workup procedures very simple. The catalyst can easily be recovered after the reaction and reused without the significant loss of the catalytic activity and selectivity. However, leaching and/or deactivation problems of the heterogeneous catalysts are responsible for severe drawbacks and are frequently observed in many cases. The following control experiments were carried out in order to verify whether the observed catalysis is caused by the solid $Rh(OH)_x/Al_2O_3$ or leached rhodium species. After the catalytic transformation of 1a to benzamide was completed under the conditions described in Table 1, the $Rh(OH)_x/Al_2O_3$ catalyst and benzamide were removed by filtration. The substrate was then added to the filtrate and the mixture was again heated to the reaction temperature. The corresponding benzamide was not formed. It was confirmed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis that the amount of rhodium species in the filtrate was below the detection limit (Rh: <0.25%). These observations can rule out any contribution to the observed catalysis from rhodium species that leached into the reaction solution, and the observed catalysis is truly heterogeneous in nature.[18]

Mechanistic Studies

The reaction profiles for the transformation of 1a to benzamide showed that benzonitrile was initially formed followed by the formation of benzamide. Furthermore, the dehydration of benzamide to benzonitrile hardly proceeded under the same conditions, showing that benzonitrile is produced only from starting with 1a. It was confirmed in a separate experiment that the hydration of nitriles to amides efficiently proceeded in the presence of the $Rh(OH)_x/Al_2O_3$ catalyst. The hydration of p-chlorobenzonitrile readily proceeded to give p-chlorobenzamide in an isolated yield of 72% [Eq. (4)]. Therefore, the transformation of aldoximes to primary amides proceeds by sequential reactions, namely, the dehydration of aldoximes to nitriles followed by rehydration to afford the corresponding primary amides.

$$(4)$$
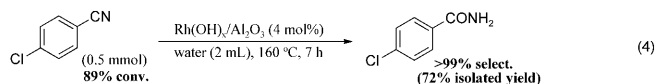
The reaction of ketoximes such as cyclohexanone oxime and acetophenone oxime did not proceed, suggesting that the $Rh(OH)_x/Al_2O_3$-catalyzed transformation proceeds by a different way as compared to the acid-catalyzed Beckmann rearrangement.[2] Furthermore, the O-alkylated aldoxime of O-methylbenzaldoxime did not react under the present conditions. These results suggest that both OH and H function-

alities of aldoximes play important roles in the present transformation. It is probable that the OH groups of aldoximes ligate to the rhodium center followed by the elimination of H^+ to produce nitriles as intermediates. A similar mechanism has been proposed for the rhenium-catalyzed dehydration of aldoximes to nitriles.[17]

Next, the competitive hydration of benzonitrile and p-substituted benzonitriles was carried out under the conditions described in Table 1. The reactivity for benzonitriles changed in the order of p-OMe ($k_X/k_H = 1.35$) > p-Me (1.16) > p-H (1.00) > p-Cl (0.96). The linear line of the Hammett plots ($\log(k_X/k_H)$ versus Brown-Okamoto σ^+ plots, $r^2 = 0.99$, Figure 3) gave a Hammett ρ value of -0.17. In
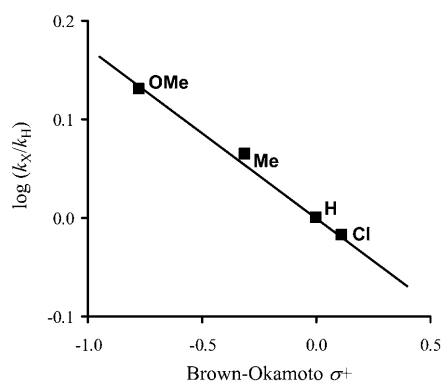

Figure 3. Hammett plots for the competitive reaction of benzaldoximes under the conditions described in Table 1. Slope (the Hammett ρ value) = -0.17 ($r^2 = 0.99$).

contrast to the negative ρ value for the $Rh(OH)_x/Al_2O_3$-catalyzed hydration, the ρ value for the NaOH-mediated hydration (external attack of a free OH^- species (or water) to a nonactivated nitrile carbon) is positive, indicating the formation of a negatively charged transition state.[20] Therefore, a free OH^- species is not an active species for the hydration. The negative ρ value might arise from the formation of a positively charged transition state at the carbon atom adjacent to the phenyl ring,[20] for instance, the activation of nitriles by coordination to the Lewis acid center is kinetically important.[12,18] The steric effect[11d] mentioned above also supports this idea.

The reaction rate for the dehydrative condensation of benzaldehyde and hydroxylamine in the presence of $Rh(OH)_x/Al_2O_3$ was $1.5\ mM\,min^{-1}$ at 80 °C and was much faster in the absence of the catalyst ($0.035\ mM\,min^{-1}$), showing that $Rh(OH)_x/Al_2O_3$ catalyzes not only the amide formation (sequential dehydration-rehydration) but also the dehydrative condensation of aldehydes and hydroxylamine.

On the basis of these results, we propose a possible reaction mechanism for the $Rh(OH)_x/Al_2O_3$-catalyzed synthesis of primary amides. The dehydrative condensation of aldehydes with hydroxylamine is promoted by the $Rh(OH)_x/Al_2O_3$ catalyst (Brønsted base catalysis, Scheme 1a). The OH groups of aldoximes bind to the rhodium center by a

ligand exchange to form the Rh−O−N=CHR species, which then eliminate the H^+ to afford nitriles as intermediates and the starting Rh−OH species (Scheme 1b). The nitrile hydration likely proceeds as shown in Scheme 1c.[11d] The coordination of nitriles to the rhodium center is followed by the intramolecular nucleophilic attack of the hydroxide species on the nitrile carbons to give the rhodium iminolate or η^2-amidate species.[12] The ligand exchange between the intermediates and water then takes place to afford the corresponding primary amides and the starting Rh−OH species.

Conclusions

A supported rhodium hydroxide, $Rh(OH)_x/Al_2O_3$ acts as an efficient heterogeneous catalyst for the synthesis of primary amides from aldoximes or aldehydes in water. The reaction of both activated and nonactivated substrates proceeds with high efficiency to afford the corresponding primary amides. The present system has the following significant advantages: 1) applicability to various kinds of substrates; 2) the use of only one equivalent of hydroxylamine in the case of the tandem synthesis of primary amides from aldehydes; 3) the use of water as a solvent; 4) simple workup procedures, namely, catalyst/product separation; 5) reusability of $Rh(OH)_x/Al_2O_3$; and 6) the use of easily prepared $Rh(OH)_x/Al_2O_3$ catalyst and handling.

Experimental Section

General

GC analyses were performed on a Shimadzu GC-2014 device with a flame ionization detector (FID) equipped with a TC-1 or TC-5 capillary column. Mass spectra were recorded on a Shimadzu GC–MS-QP2010 spectrometer at an ionization voltage of 70 eV. The liquid-state NMR spectra were recorded on a JEOL JNM-EX-270 spectrometer. ^{1}H and ^{13}C NMR spectra were measured at 270 and 67.8 MHz, respectively, with TMS as an internal standard. IR spectra were recorded on a JASCO FTIR-460 Plus spectrometer. ESR measurements (X-band) were performed with a JEOL JES-RE-1X. XRD patterns were measured with a Rigaku MultiFlex diffractometer using $Cu_{K\alpha}$ radiation (40 kV, 50 mA). XPS measurements were carried out on a JEOL JPS-90 spectrometer using monochromated $Al_{K\alpha}$ 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 10.0 eV to ensure sufficient resolution to determine peak positions accurately. The binding energies were calibrated by using the C 1s signal at 285.0 eV. The X-ray absorption spectra were recorded at the NW10A beamline of PF at KEK, Japan (proposal No. 2007G096). Data analysis was performed using REX2000 software (version 2.5, Rigaku). The ICP-AES analysis was performed with a Shimadzu ICPS-8100 spectrophotometer.

Alumina (KHS-24, BET surface area: $174\ m^2\,g^{-1}$) was supplied from Sumitomo Chemical Co., Ltd. Solvents, aldehydes, and **1a** were obtained from Tokyo Kasei or Aldrich (reagent grade) and purified prior to use.[21] $RhCl_3\cdot3H_2O$ was obtained from Wako (reagent grade) and used as received. $NH_2OH\cdot HCl$ and $(NH_2OH)_2\cdot H_2SO_4$ were obtained from Tokyo Kasei (reagent grade) and used as received.

Synthesis of Aldoximes

Aldoximes (**2a**–**16a**) were synthesized by the dehydrative condensation of the corresponding aldehydes with $NH_2OH\cdot HCl$.[6] Into a glass flask

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were successively placed an aldehyde (10 mmol), $NH_2OH \cdot HCl$ (2–3 equivalents with respect to the aldehyde), ethanol (10 mL), and pyridine (1 mL). The reaction mixture was stirred at room temperature. After completion of the reaction, ethanol was removed under reduced pressure on a rotary evaporator. Then, deionized water (ca. 10 mL) was added to the residue and the mixture was cooled in an ice-bath until the aldoxime crystallized out (except for **9a**, **10a**, **12a**, and **14a**). The aldoxime was filtered, washed with deionized water (ca. 100 mL), dried, and recrystallized from ethanol. For **9a**, **10a**, **12a**, and **14a**, aldoximes were extracted into dichloromethane and purified by Kugelrohr distillation. All aldoximes were confirmed by mass and NMR spectroscopy.[6] The *E/Z* ratios of aldoximes are listed in Table 1.

Dehydrative Condensation of Aldehydes with Hydroxylamine

Into a glass vial were successively placed $Rh(OH)_x/Al_2O_3$ (Rh: 2 mol %), $NH_2OH \cdot HCl$ (2 mmol), benzaldehyde (1 mmol), and *o*-xylene (3 mL). The reaction mixture was stirred at 80 °C under Ar at 1 atm. The conversion and yield were periodically determined by GC analysis. Reaction rates were determined from the slopes of reaction profiles ([benzaldehyde]$_0$–[benzaldehyde]$_t$ vs. time plots) at low conversions (< 10 %) of benzaldehyde (initial rate method).

Synthesis of Amides from Aldoximes or Aldehyde

An aldoxime or aldehyde (0.5 mmol, in the case of an aldehyde, one equivalent of $(NH_2OH)_2 \cdot H_2SO_4$ (0.25 mmol) was added), $Rh(OH)_x/Al_2O_3$ (Rh: 4 mol %), and water (2 mL) were placed in a teflon vessel with a magnetic stir bar. The teflon vessel was attached inside an autoclave, and then the autoclave was heated at 120–160 °C (bath temperature). After the reaction was completed, the spent catalyst was separated by filtration, washed with ethanol, and dried in vacuo prior to being recycled. The products (amides) were isolated by silica gel column chromatography using ethanol as an eluent. The products were confirmed by the comparison of their GC retention time, mass, and ^1H and ^{13}C NMR spectroscopy with those of authentic samples.

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[16] Al_2O_3 was the most suitable support for the synthesis of primary amides. When more acidic supports such as SiO_2 and TiO_2 were used, the selectivity to primary amides decreased (70–80 %) because of the decomposition of aldoximes to aldehydes.

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