

## Catalytic Amide Synthesis

## A One-Pot Synthesis of Primary Amides from Aldoximes or Aldehydes in Water in the Presence of a Supported Rhodium Catalyst\*\*

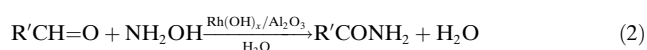
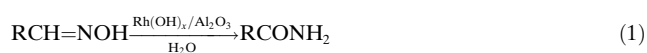
Hiroshi Fujiwara, Yoshiyuki Ogasawara, Kazuya Yamaguchi, and Noritaka Mizuno\*

The development of efficient methods for the synthesis of amides is very important because of their usefulness in a wide variety of applications in academia and industry, especially as intermediates in organic synthesis, raw materials for engineering plastics, detergents, and lubricants.<sup>[1]</sup> The conversion of carbonyl compounds, such as aldehydes, ketones, and oximes, is a good candidate for the synthesis of amides. For example, the Beckmann rearrangement is commonly used to transform ketoximes (RR'C=NOH) into the corresponding N-substituted amides (RCONHR') even though it generally requires the use of strong acids under severe reaction conditions.<sup>[2]</sup> The equivalent reaction with aldoximes (RCH=NOH), however, gives the corresponding nitriles (RCN) rather than primary amides (RCONH<sub>2</sub>) as the H atom acts as a leaving group.

The synthesis of primary amides from aldoximes is very difficult and reactive reagents have to be used in stoichiometric amounts for the transformation to occur.<sup>[3]</sup> In addition, the selectivities for the desired amides are often very low with reactive stoichiometric reagents because undesired nitriles, carboxylic acids, and aldehydes are formed in some cases.<sup>[3]</sup> This situation is a severe drawback for scaling up and industrial applications. To our knowledge, only four catalytic examples of this transformation have been reported and these systems homogeneously catalyze the transformation in organic solvents.<sup>[4]</sup> The development of environmentally and technologically desirable, heterogeneously catalyzed procedures for this process remains a great challenge.<sup>[5]</sup>

Herein we report that the easily prepared supported rhodium hydroxide (Rh(OH)<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub>) acts as an effective heterogeneous catalyst for the one-pot synthesis of primary amides from various kinds of aldoximes in water—in the complete absence of explosive, hazardous, and carcinogenic organic solvents [Eq. (1)].<sup>[6]</sup> The Rh(OH)<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst can easily be recovered by filtration and reused with retention of its high catalytic performance. The catalysis is truly heterogeneous because the filtrate is completely inactive after the

solid catalyst is removed. Furthermore, Rh(OH)<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> can be applied to the one-pot synthesis of primary amides from the corresponding aldehydes and hydroxylamine [Eq. (2)]. To our knowledge, the heterogeneously catalyzed one-pot transformation of aldoximes and aldehydes into amides in water has not been reported to date.



The scope of this Rh(OH)<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub>-catalyzed system towards structurally diverse aldoximes was examined first. No amides were produced in the absence of the catalyst or in the presence of Al<sub>2</sub>O<sub>3</sub> or Rh<sub>2</sub>O<sub>3</sub> on their own. The selectivities for the corresponding amides were low with the catalyst precursor RhCl<sub>3</sub>·3H<sub>2</sub>O.<sup>[7]</sup> Rh(OH)<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> showed high catalytic activity for the transformation of unactivated, activated, unsaturated, and heteroatom-containing aldoximes (Table 1). Unactivated aliphatic aldoximes, including linear (**1a** and **2a**), branched (**3a** and **4a**), and cyclic (**5a**) substrates, were converted into the corresponding aliphatic amides in excellent yields (entries 1–6, Table 1), and benzaldoximes (**6a–10a**) were smoothly converted into benzamides in high yields (entries 7–12, Table 1). The reaction with unsaturated aldoximes such as *trans*-cinnamaldoxime (**11a**) and *cis*-8-undecenaloxime (**12a**) proceeded efficiently to afford the corresponding unsaturated amides with no isomerization of the alkene double bond (entries 13 and 14, respectively, Table 1). The presence of heteroatoms, including sulfur (**13a**) and oxygen (**14a**), in the substrate did not alter the conversion or selectivity, and the corresponding amides were obtained in excellent yields (entries 15 and 16, respectively, Table 1).

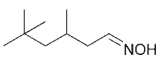
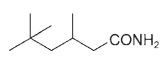
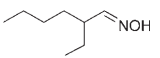
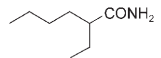
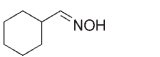
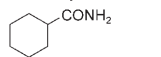
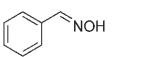
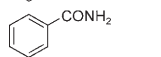
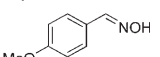
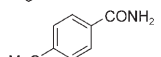
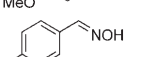
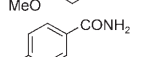
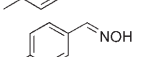
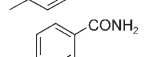
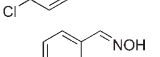
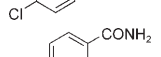
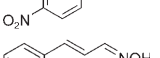
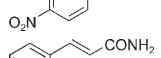
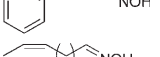
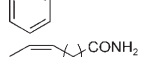
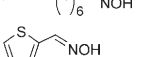
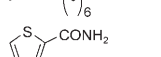
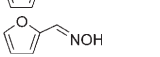
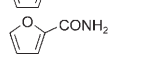
It is important to verify that the observed catalytic conversion is caused by solid Rh(OH)<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> rather than leached rhodium species, therefore the following control experiments were carried out. A catalytic transformation of **6a** was carried out under the conditions in Table 1. After complete consumption of **6a**, Rh(OH)<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> and the product (**6b**) were removed from the reaction mixture by filtration. When further substrate was added to the filtrate, and the mixture was again heated at 160 °C, no production of amide was observed. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) showed that the amount of rhodium species present in the filtrate was below the detection limit (<0.25%). Furthermore, the Rh(OH)<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst could be reused with the same catalytic performance (entries 2 and 8 in Table 1). These findings rule out any contribution to the observed catalytic conversion

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[\*\*] This work was supported by the Core Research for Evolutional Science and Technology (CREST) program of the Japan Science and Technology Agency (JST) and a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Science, Sports and Technology of Japan. We are grateful to Ms. M. Kotani (JST) for her help with the experimental work.

Supporting Information for this article is available on the WWW under <http://www.angewandte.org> or from the author.

**Table 1:** The synthesis of amides from aldoximes catalyzed by  $\text{Rh}(\text{OH})_x/\text{Al}_2\text{O}_3$ .<sup>[a]</sup>

Entry	Substrate	Product	Conv. [%]	Sel. [%]
1 <sup>[b]</sup> 2 <sup>[b,c]</sup>	$n\text{-C}_{11}\text{H}_{23}\text{CH}=\text{NOH}$ <b>1a</b>	$n\text{-C}_{11}\text{H}_{23}\text{CONH}_2$ <b>1b</b>	> 99 > 99	93(84) 91
3 <sup>[b]</sup>	$n\text{-C}_7\text{H}_{15}\text{CH}=\text{NOH}$ <b>2a</b>	$n\text{-C}_7\text{H}_{15}\text{CONH}_2$ <b>2b</b>	> 99	98(83)
4 <sup>[b]</sup>	 <b>3a</b>	 <b>3b</b>	> 99	99(86)
5 <sup>[b]</sup>	 <b>4a</b>	 <b>4b</b>	> 99	96(86)
6 <sup>[b]</sup>	 <b>5a</b>	 <b>5b</b>	87	88(63)
7 8 <sup>[c]</sup>	 <b>6a</b>	 <b>6b</b>	> 99 94	85(76) 81
9	 <b>7a</b>	 <b>7b</b>	> 99	85(88)
10	 <b>8a</b>	 <b>8b</b>	> 99	97(77)
11	 <b>9a</b>	 <b>9b</b>	> 99	95(87)
12	 <b>10a</b>	 <b>10b</b>	> 99	92(90)
13	 <b>11a</b>	 <b>11b</b>	> 99	92(70)
14 <sup>[b]</sup>	 <b>12a</b>	 <b>12b</b>	96	97(92)
15	 <b>13a</b>	 <b>13b</b>	> 99	96(84)
16	 <b>14a</b>	 <b>14b</b>	93	98(71)

[a] Reaction conditions: aldoxime (0.5 mmol),  $\text{Rh}(\text{OH})_x/\text{Al}_2\text{O}_3$  (4 mol% Rh), water (2 mL), 7 h, 160 °C. Nitriles and aldehydes were formed as by-products (see the Supporting Information). The values in parentheses are yields of isolated products. [b] Reaction temperature: 140 °C. [c] Catalyst reused.

from rhodium species that leach into the reaction solution, which means that this catalyst is truly heterogeneous.<sup>[8]</sup>

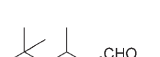
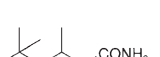
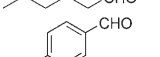
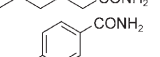
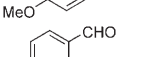
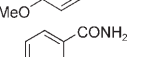
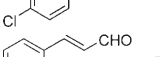
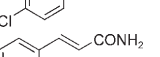
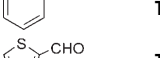
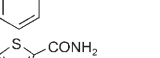
The  $\text{Rh}(\text{OH})_x/\text{Al}_2\text{O}_3$  catalyst was also applied to the one-pot synthesis of amides from hydroxylamine and an aldehyde.<sup>[9]</sup> Various kinds of aldehydes, including aliphatic (**1c** and **3c**), aromatic (**7c** and **9c**), unsaturated (**11c**), and heterocyclic (**13c**) ones, could be converted into the corresponding amides in high yields in the presence of only one equivalent of hydroxylamine with respect to the aldehyde (Table 2). This reaction is also catalyzed heterogeneously and the  $\text{Rh}(\text{OH})_x/\text{Al}_2\text{O}_3$  catalyst could be reused without significant loss of catalytic activity. Although the tandem one-pot synthesis of amides is very useful, stoichiometric amounts of reagents such as  $\text{CH}_3\text{SO}_3\text{H}$  (30 equiv with respect to substrates),  $\text{CH}_3\text{SO}_2\text{Cl}$  (1 equiv), and  $\text{ZnO}$  (2 equiv) have generally been used with an excess of hydroxylamine (> 3 equiv).<sup>[10]</sup> While Williams and co-workers have reported an efficient multi-step synthesis of amides from alcohols in the presence of  $[\{\text{Ir}(\text{Cp}^*)\text{Cl}_2\}_2]$  ( $\text{Cp}^* = \text{C}_5\text{Me}_5$ ),<sup>[4d]</sup> this homogeneous system only gives high yields of amides in the presence of an additive, such as  $\text{Cs}_2\text{CO}_3$  (2 equiv with respect to Ir) or styrene (hydrogen acceptor, 1.5 equiv with respect to substrates). In contrast, the present system has the following significant advantages: 1) applicability to various kinds of substrates, 2) the need for only one equivalent of hydroxyl-

amine, 3) the use of water as solvent, 4) a simple workup procedure, namely catalyst/product separation by filtration, 5) reusability of the  $\text{Rh}(\text{OH})_x/\text{Al}_2\text{O}_3$  catalyst, and 6) the use of an easily prepared  $\text{Rh}(\text{OH})_x/\text{Al}_2\text{O}_3$  catalyst that is easy to handle.

Nitriles are formed as by-products in this one-pot transformation, albeit in only small amounts with most of the substrates tested (around 9%, see the Supporting Information). The dehydration of amides to nitriles did not proceed at all under the present conditions, which shows that the nitriles are derived only from the starting aldoximes as the primary products and subsequent hydration of nitriles to amides then occurs. A separate experiment confirmed that  $\text{Rh}(\text{OH})_x/\text{Al}_2\text{O}_3$  efficiently catalyzes the hydration of nitriles to amides,<sup>[11]</sup> therefore the present transformation of aldoximes to amides most likely proceeds by sequential dehydration/hydration reactions, that is, the dehydration of aldoximes to nitriles followed by their hydration to give the corresponding amides.

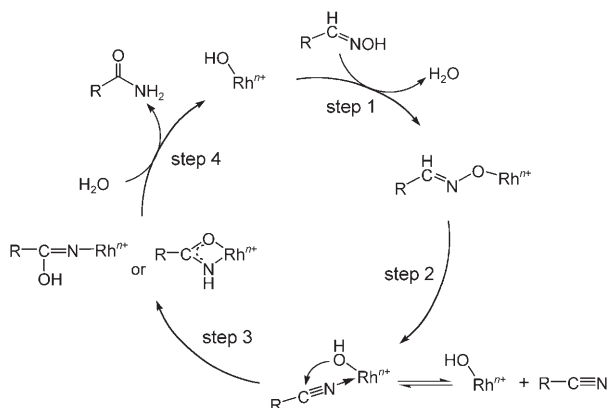
The O-alkylated aldoxime *O*-methylbenzaldehyde and ketoximes such as cyclohexanone oxime and acetophenone oxime did not react under the same conditions as in Table 1. This

**Table 2:** The synthesis of amides from aldehydes catalyzed by  $\text{Rh}(\text{OH})_x/\text{Al}_2\text{O}_3$ .<sup>[a]</sup>

Entry	Substrate	Product	Conv. [%]	Sel. [%]
1 <sup>[b,c]</sup>	$n\text{-C}_{11}\text{H}_{23}\text{CH}=\text{O}$ <b>1c</b>	$n\text{-C}_{11}\text{H}_{23}\text{CONH}_2$ <b>1b</b>	> 99	89(89)
2 <sup>[c]</sup>	 <b>3c</b>	 <b>3b</b>	> 99	91(81)
3	 <b>7c</b>	 <b>7b</b>	98	86(90)
4	 <b>9c</b>	 <b>9b</b>	98	94(85)
5	 <b>11c</b>	 <b>11b</b>	99	88(73)
6	 <b>13c</b>	 <b>13b</b>	99	99(85)

[a] Reaction conditions: aldehyde (0.5 mmol),  $(\text{NH}_2\text{OH})_2\cdot\text{H}_2\text{SO}_4$  (0.25 mmol, 1 equiv with respect to aldehyde),  $\text{Rh}(\text{OH})_x/\text{Al}_2\text{O}_3$  (4 mol% Rh), water (2 mL), 7 h, 160 °C. Nitriles, aldoximes, and carboxylic acids were formed as by-products (see the Supporting Information). The values in parentheses are yields of isolated products. [b] Reaction time: 9 h. [c] Reaction temperature: 120 °C.

suggests that both OH and H functionalities play an important role in this transformation. It is probable that the OH groups of aldoximes bind to the rhodium center to form Rh–O–N=CHR species (step 1 in Scheme 1), which then eliminate H<sup>+</sup> to give nitrile intermediates and the starting Rh–OH species (step 2 in Scheme 1).<sup>[12]</sup> The Rh(OH)<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub>-catalyzed hydration of nitriles likely proceeds by a mechanism



**Scheme 1.** A possible reaction mechanism for the conversion of aldoximes into amides. The value of  $n$  is probably 3.

similar to that of a previously reported Ru(OH)<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub>-catalyzed hydration (steps 3 and 4 in Scheme 1).<sup>[13]</sup> The reaction rate is independent of the concentration of D<sub>2</sub>O, which indicates that O–H bond dissociation is not the rate-limiting step. The reaction of **6a** (PhCH=NOH) and  $\alpha$ -deuteriobenzaldoxime (PhCD=NOH) gave a kinetic isotope effect ( $k_H/k_D$ ) of  $3.1 \pm 0.4$  under the conditions described in Table 1, which suggests that C–H bond cleavage (step 2 in scheme 1) is the rate-limiting step.<sup>[14]</sup>

In summary, Rh(OH)<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> is an efficient heterogeneous catalyst for the one-pot synthesis of primary amides from activated and unactivated aldoximes or aldehydes in water in high yields.

## Experimental Section

The Rh(OH)<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst was prepared as follows. Powdered Al<sub>2</sub>O<sub>3</sub> (KHS-24, supplied by Sumitomo Chemical Co., Ltd.; BET surface area: 160 m<sup>2</sup> g<sup>-1</sup>; 2.0 g) was calcined at 550 °C for 3 h and was then vigorously stirred with 60 mL of an aqueous solution of RhCl<sub>3</sub> (6.5 mM) at room temperature. After 15 min, the pH value of the solution was quickly adjusted to 13 with an aqueous solution of NaOH (1.0 M) and the resulting slurry was stirred for 24 h at room temperature. The solid was then collected by filtration, washed with a large volume of deionized water, and dried in vacuo to afford 2.0 g of Rh(OH)<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> as a yellow powder with a rhodium content of 2.1 wt%. The rhodium content can be varied by changing the concentration of the starting rhodium solution. The IR spectrum of Rh(OH)<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> shows a broad  $\nu$ (OH) band in the range 3000–3770 cm<sup>-1</sup>. The XRD pattern of Rh(OH)<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> was the same as that of the parent Al<sub>2</sub>O<sub>3</sub> support and no peaks for rhodium metal (clusters) or rhodium oxides were observed.<sup>[15]</sup> The X-ray photoelectron spectrum of Rh(OH)<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> showed Rh3d<sub>5/2</sub> and Rh3d<sub>3/2</sub> binding energies of 310.0 (full width at half maximum (FWHM): 1.4 eV) and 314.8 eV (FWHM: 1.4 eV), respectively, which indicate that the

oxidation state of rhodium species is possibly +3.<sup>[16]</sup> The Rh(OH)<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst is ESR silent. All these results suggest that rhodium(III) hydroxide is highly dispersed on Al<sub>2</sub>O<sub>3</sub>. A detailed characterization of Rh(OH)<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> is in progress.

A typical Rh(OH)<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub>-catalyzed synthesis of amides is as follows: *n*-Dodecanaldoxime (0.5 mmol), Rh(OH)<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> (4 mol% Rh), and water (2 mL) were placed in a Teflon vessel along with a magnetic stir bar. The Teflon vessel was placed inside an autoclave and heated at 140 °C (bath temperature). After the reaction had finished, the spent catalyst was separated by filtration, washed with ethanol, and dried in vacuo prior to being reused. The products (amides) were isolated by silica gel column chromatography with ethanol as eluent. Amides were efficiently produced from aldoximes and aldehydes in water, whereas nitriles were the major products in common organic solvents such as toluene and *o*-xylene. The identity of the products was confirmed by comparison of their GC retention times, mass spectra, and <sup>1</sup>H and <sup>13</sup>C NMR spectra with those of authentic samples.

Received: March 23, 2007

Published online: May 30, 2007

**Keywords:** aldehydes · amides · heterogeneous catalysis · rhodium · supported catalysts

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