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Selective Hydrogenation of Amides to Alcohols in Water Solvent over Heterogeneous CeO_2-Supported Ru Catalyst

Masazumi Tamura* Susumu Ishikawa, Mii Betchaku, Yoshinao Nakagawa, Keiichi Tomishige*

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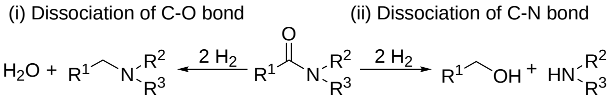
CeO_2-suppoeted Ru (Ru/CeO_2) worked as an effective and reusable heterogeneous catalyst for selective dissociation of the C-N bond in amides, particularly primary amides, with H_2 in water solvent under low reaction temperature of 333 K, and high yields of the corresponding alcohols were obtained from primary amides.

Amides are ubiquitous in nature as polypeptides of proteins and can be found in a wide range of chemicals such as polyamides (typically nylons), agrochemicals and pharmaceuticals and so on. Reductive transformation of amides is one of important organic reactions [1], and there are two pathways (Scheme 1): (i) Transformation of amides to amines via dissociation of the C-O bond; (ii) Transformation of amides to alcohols and amines (or ammonia) via dissociation of the C-N bond. Reduction transformation of amides is generally difficult due to low electrophilicity of the carbonyl carbon in amides[2]. Conventionally, stoichiometric reducing agents such as metal hydrides are used for C-O bond scission, and aminoborohydrides[3] and SmI_2[4] are effective reducing agents for C-N bond scission in amides. However, these systems have some drawbacks such as high cost of reductants and production of large amount of salts. As an alternative method, catalytic reduction with cheap reducing agents such as H_2 is desirable. Various homogeneous[5] and heterogeneous[6] catalysts have been intensively developed for the route (i). As for the route (ii), various Ru[7], Fe[8] and Mn[9] complexes were reported to be effective, however, most of these catalysts required additives such as strong bases, use of organic solvents, and high temperature (typically ≥353 K). Moreover, application to primary amides is commonly difficult because of the free NH bonds[4a], and the yields were very low (0~74%). Recently, Saito and co-workers substantiated effective transformation of benzamide to benzyl alcohol in high yield of 92% by using Ru complex ((P,(N,N)$_{bpy}$, P)Ru)[7j], although the catalyst system required high temperature (433 K), toluene solvent and strong base (NaH). When our manuscript was submitted, there are no reports on heterogeneous catalysts developed for C-N bond scission in amides, and the reported highest yield from amides to alcohols over heterogeneous catalysts is very low (27%). During the review of our manuscript, outstanding result on selective hydrogenation of C-N bonds in amides over heterogeneous Ag/Al_2O_3 catalyst was published by Milstein and co-workers[10]. The catalyst system was effective for secondary amides and provided high yield of corresponding alcohols and amines (up to 99%), however suffered from use of strong bases such as *t*-BuOK, high temperature (423 K), use of organic solvent (1,4-dioxane) and low yield from primary amides (61%). Therefore, development of effective heterogeneous catalysts for reductive transformation of amides, particularly primary amides, to alcohols and amines under mild reaction conditions is desirable. Herein, we found that Ru/CeO_2 was an effective heterogeneous catalyst for selective C-N bond dissociation of amides, particularly primary amides.



Scheme 1. Reductive transformation of amides

Catalytic performance for hydrogenation of amides was investigated by hydrogenation of cyclohexanecarboxamide in water solvent at 333 K and 8 MPa H_2 as a model reaction (Table 1). No reaction was observed in the absence of catalysts (entry 17). At first, various carbon-supported noble metal catalysts were applied to the reaction (entries 1-4). Ru/C showed much higher conversion than the other carbon-supported catalysts, and the selectivity to cyclohexanemethanol (**1**) was high (90%), while Rh/C showed high selectivity to cyclohexanemethylamine (**2**). Next, effect of supports in Ru catalysts was investigated by using various metal oxide supports (Table 1, entries 5-11). All

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[a] Graduate School of Engineering, Tohoku University, Aoba 6-6-07, Aramaki, Aoba-ku, Sendai, 980-8579 (Japan). Email: mtamura@erec.che.tohoku.ac.jp, tomi@erec.che.tohoku.ac.jp

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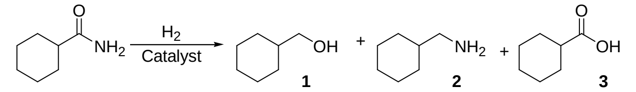
Table 1. Hydrogenation of cyclohexanecarboxamide over various catalysts



Entry	Catalyst	Conv. (%)	Selectivity (%)			
			1	2	3	Others
1	Ru/C[a]	30	90	7.5	<0.1	3.1
2	Rh/C[a]	3.5	29	63	<0.1	7.8
3	Pt/C[a]	0.3	77	<0.1	<0.1	23
4	Pd/C[a]	0.3	28	<0.1	28	34
5	Ru/CeO_2	52	97	0.2	0.8	2.0
6	Ru/SiO_2	40	99	<0.1	0.2	0.9
7	Ru/ZrO_2	33	98	<0.1	1.7	0.9
8	Ru/TiO_2	27	96	<0.1	3.3	1.1
9	Ru/SiO_2-Al_2O_3	22	98	1.4	0.4	0.8
10	Ru/γ-Al_2O_3	18	98	0.0	0.7	0.9
11	Ru/MgO	16	92	7.6	<0.1	0.5
12	Rh/CeO_2	6.2	56	1.5	4.3	38
13	Pt/CeO_2	0.3	38	<0.1	62	<0.1
14	Ir/CeO_2	0.3	42	<0.1	58	<0.1
15	Pd/CeO_2	0.2	46	<0.1	54	<0.1
16	CeO_2	0.6	<0.1	<0.1	>99	<0.1
17	-	<0.1	-	-	-	-

Reaction conditions: catalyst 0.50 g (metal: 4 wt%) [a]0.4 g (metal: 5 wt%), cyclohexanecarboxamide 1.5 mmol, water 20 ml, H_2 8 MPa, 333 K, 4 h. Others include cyclohexane, methylcyclohexane and methane.

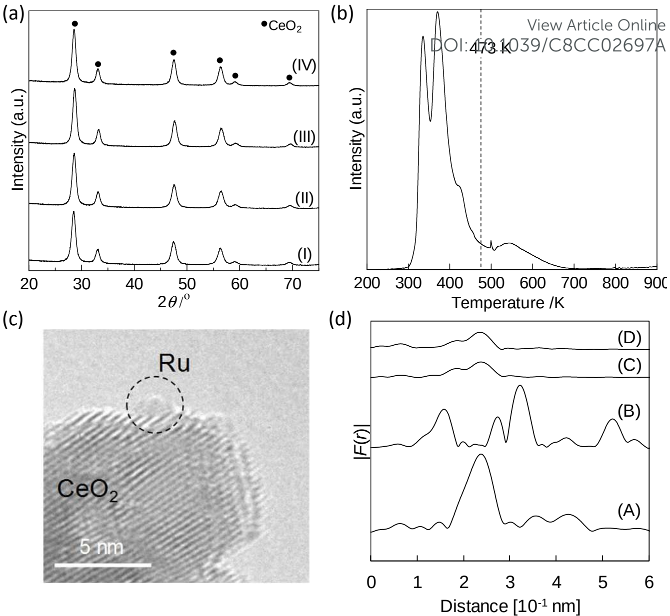


Figure 1. Characterization of Ru/CeO_2 catalysts. (a) XRD patterns of CeO_2 and Ru/CeO_2 catalysts ((I) CeO_2, (II) Ru/CeO_2 after calcination, (III) Ru/CeO_2 after reduction, (IV) Ru/CeO_2 after 24 h reaction), (b) TPR analysis of Ru/CeO_2. (c) TEM image of Ru/CeO_2 after reduction, (d) Fourier transform of k^3-weighted Ru *K*-edge EXAFS analyses ((A) Ru powder, (B) RuO_2, (C) Ru/CeO_2 after reduction, (D) Ru/CeO_2 after 48 h reaction), FT range 30-120 nm^{-1}.

supported Ru catalysts showed high selectivity to **1** (92-99%) with moderate to low conversion (16-52%), and Ru/CeO_2 showed higher conversion than the other Ru catalysts. Only CeO_2 had almost no activity for the reaction (entry 16). Performance of CeO_2-supported noble metal catalysts was compared in the same reaction (Table 1, entries 5 and 12-15). The CeO_2-supported noble metal catalysts except Ru/CeO_2 showed low conversion (< 10%) and low selectivity to **1** (< 60%). As above, combination of CeO_2 and Ru was the most effective for the reaction. The performance of Ru/CeO_2 catalysts with different Ru loading amounts was compared in the same reaction with the same Ru amount by adjusting the introduced catalyst amount (0.20 mmol, Table S1). The conversion gradually increased with increasing the Ru loading amount up to 4 wt%, and the conversion gradually decreased with increasing Ru loading amount more than 4 wt%, although the difference of the conversions is not so large. The selectivities to **1** were similar (94-98%). Therefore, 4 wt% Ru supported CeO_2 catalyst was selected as an optimized one.

Ru/CeO_2 (Ru: 4 wt%) catalyst was characterized by XRD, TPR, TEM and XAS (Figure 1, Figures S1 and S2, and Table S2). XRD patterns of Ru/CeO_2 catalysts after calcination, reduction and reaction are almost the same as that of CeO_2, and signals due to Ru species (Ru metal: main peak (101) at ~44°, RuO_x: main peak (101) at ~35°) were not detected (Figure 1(a)), which implies that Ru species are highly dispersed. TPR profile of Ru/CeO_2 is shown in Figure 1(b). Based on the reduction temperature of 473 K, the consumed H_2 amount below 473 K is calculated to be 1.6 mmol/g. Considering that the consumed H_2 amount is much larger than Ru metal amount (0.4 mmol/g,), Ru species on CeO_2 is reduced to Ru metal and a part of CeO_2 was also reduced. CO adsorption analysis confirmed high dispersion of Ru metal species (H/Ru=0.92), suggesting that Ru metal species are highly dispersed and the particle size of Ru metal species is very small. TEM image of Ru/CeO_2 provided small Ru particles (~1.5 nm) (Figure 1(c)), and much smaller particles will not be found due to low contrast between CeO_2 and Ru particles. XAS analyses of Ru/CeO_2 catalysts after reduction and reaction were carried out (Figure 1(d), and Figures S1 and S2 and Table S2). Ru *K*-edge XANES spectra of Ru/CeO_2 catalyst are similar to that of Ru powder (Figure S1). Fourier transform of k^3-weighted Ru *K*-edge EXAFS of Ru/CeO_2 showed the signal corresponding to Ru metal (Figure 1(d)), and the curve-fitting analysis provided the presence of Ru-Ru bond with a coordination number (CN) of ~5 (Figures S1 and S2, and Table S2). These results indicate that Ru species on CeO_2 was in the metallic state, which is good accordance with TPR analysis. Based on the CN of Ru-Ru, Ru species are subnanocluster[11], which agrees with the results of XRD, CO-adsorption and TEM analyses.

Reaction parameters such as reaction temperature, H_2 pressure, substrate concentration and solvent were investigated in the same reaction with Ru/CeO_2 catalyst (Tables S3-S6). Effect of reaction temperature was studied at the range from 313 to 413 K (Table S3). The conversion increased with increasing the reaction temperature, however, the selectivity to **1** drastically decreased at higher temperatures than 333 K, and those to cyclohexanecarboxylic acid (**3**) and others increased. In terms of activity and selectivity, 333 K was selected for the following study. Solvents often affect the activity and selectivity. The reactions were conducted with various polar solvents such as water, 1,2-dimethoxyethane, THF, 2-propanol and methanol (Table S4). Among the solvents tested, water provided higher conversion than the other solvents, although the selectivity was not so different. Therefore, water was selected as the best one.

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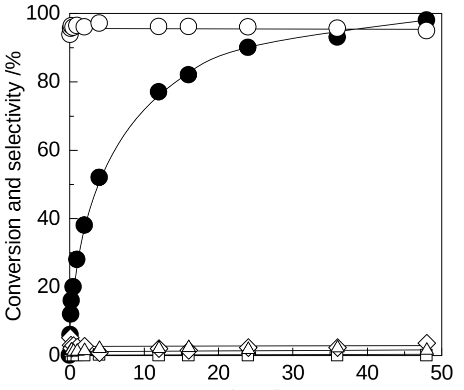


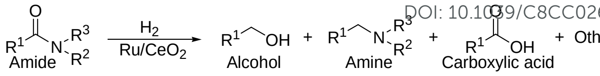
Figure 2. Time-course of hydrogenation of **1** over Ru/CeO₂ (● conversion, ○ selectivity to **1**, □ selectivity to **2**, ◇ selectivity to **3**, △ selectivity to others). Reaction conditions: Ru/CeO₂ 0.5 g (Ru: 4 wt%, 0.20 mmol), cyclohexanecarboxamide 1.5 mmol, water 20 ml, H_2 8 MPa, 333 K. Others include cyclohexane, methylcyclohexane and methane.

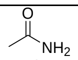
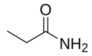
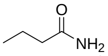
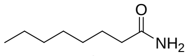
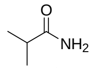
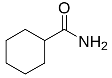
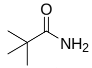
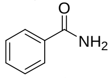
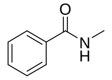
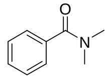
From the results of substrate concentration effect (Table S5), higher substrate concentration provided higher conversion, although the solubility of cyclohexanecarboxamide was limited. Effect of H_2 pressure was investigated at the range of 1-8 MPa (Table S6). The conversion decreased with decreasing H_2 pressure, and the selectivity to **1** also gradually decreased with decreasing H_2 pressure, and selectivities to **3** and others increased, indicating that high H_2 pressure was preferable for the reaction. Enough conversion and high selectivity were obtained even at low H_2 pressure of 2 MPa (34% conversion and 92% selectivity at 4 h and 333 K).

Time-course of hydrogenation of cyclohexanecarboxamide over Ru/CeO₂ is shown in Figure 2. The conversion increased with the reaction time to reach almost 100% conversion at 48 h. The selectivity to **1** was high (~95%) at any time, and that to **3** was almost constant (2~3%). The yield of **1** reached 93% at 48 h, which is the highest yield among the reported ones including homogeneous catalyst-based systems. The reusability of Ru/CeO₂ was studied (Figure S3). Ru/CeO₂ was reused three times without significant loss of activity and selectivity. The state of Ru metal species was not changed before and after the reaction from XAS analyses (Figure 1(d), Figure S1 and Table S2), and the structure of CeO₂ in Ru/CeO₂ was not changed from XRD analysis (Figure 1(a)). Leached amount of Ru metal species was analyzed by ICP-AES, showing that the leached amount was below the detection limit of ICP-AES (<0.05%). No contribution of leached metal species was also confirmed by leaching test (Figure S4). These results indicate that Ru/CeO₂ is a robust and reusable heterogeneous catalyst.

The scope of amides was investigated using Ru/CeO₂ catalyst (Table 2). Various linear alkyl primary amides were converted to the corresponding alcohols in high yield and selectivity (entries 1-4). Branched alkyl primary amides, isobutyramide, cyclohexanecarboxamide and pivalamide, also reacted to give the alcohols in high yields (entries 5-7). In the case of benzamide, a primary amide with a benzene ring, selective C-N bond dissociation of the amide group also occurred, although the benzene ring was hydrogenated to cyclohexane ring (entry 8). Secondary and tertiary amides, *N*-methyl benzamide, and *N,N*-dimethyl benzamide, also underwent selective C-N bond dissociation of the amide group to give the alcohols and the corresponding amount of CH_3NH_2 or $(CH_3)_2NH_2$, although the main product is the benzene ring-hydrogenated substrate (entries 9 and 10). The reactivities of secondary and tertiary amides were lower than that of primary amides, and that of the tertiary amide was lower than that of the secondary amide. The tendency will be due to the steric hindrance of the *N*-alkyl group.

Table 2. Hydrogenation of various amides over Ru/CeO₂ catalyst



Entry	Amide	Conv. (%)	C-based selectivity (%)			
			Alcohol	Amine	Carboxylic acid	Others
1		82	92	<0.1	7.8	0.2
2		93	92	<0.1	5.3	2.9
3		85	91	<0.1	6.4	2.6
4		90	80	<0.1	19	0.9
5		95	97	<0.1	3.5	<0.1
6		98	95	<0.1	3.6	1.5
7		95	99	<0.1	1.3	<0.1
8[a]		>99	92	<0.1	2.4	5.3[b]
9[a]		>99	11	<0.1	0.2	88[b,c]
10[a]		>99	5.1	<0.1	0.4	94[b,c]

Reaction conditions: Ru/CeO₂ 0.50 g, amide 1.5 mmol, water 20 ml, H_2 8 MPa, 333 K, 48 h. Others include cyclohexane, methylcyclohexane and methane. [a]Products with a cyclohexane ring. [b]Others are mainly the benzene ring-hydrogenated substrate. [c]CH_3NH_2 or $(CH_3)_2NH$ are included.

There are two possible reaction routes from amides to the corresponding alcohols (Scheme 2)[6e,7d]: (I) reaction route via formation of carboxylic acids (hydration of amides by water to carboxylic acids and sequential hydrogenation of the carboxylic acids to alcohols). (II) reaction route via formation of aldehydes (hydrogenolysis of amides to aldehydes or hydrogenation of amides to hemiaminals + deammoniation of hemiaminals to aldehydes and sequential hydrogenation of the aldehydes to alcohols). To clarify the reaction route, various related substrates were reacted with Ru/CeO₂ catalyst. To check the reaction route (I), hydrogenation of **3** was carried out at the same reaction conditions as those in hydrogenation of cyclohexanecarboxamide (Scheme 3(a)). After 24 h, the conversion was 4.9%, which is much lower than that in the case of hydrogenation of **1** (90%), indicating that the reaction route (I) is not dominant. This result is supported by the fact that hydrogenation adequately proceeded in the solvents except for water (Table S4). Therefore, the reaction route (II) will be main. Next, hydrogenation of cyclohexanecarboxaldehyde (**4**) was conducted (Scheme 3(b)). Hydrogenation of **4** proceeded very rapidly, and the conversion reached 96% in only 5 minutes.

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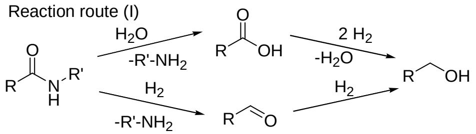
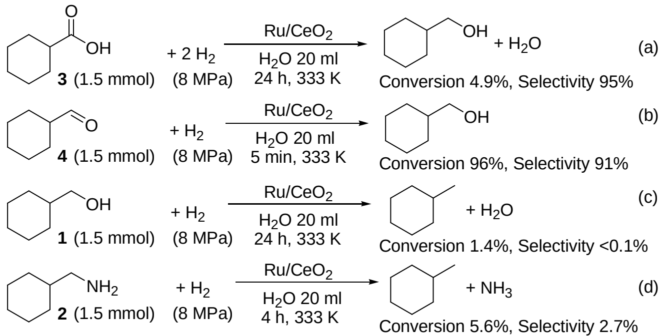
Therefore, the reaction rate is much higher than that of hydrogenation of cyclohexanecarboxamide (Figure 2), which can explain no observation of **4** in the time-course of hydrogenation of cyclohexanecarboxamide. In addition, **1** was reacted over Ru/CeO$_2$ catalyst for 24 h (Scheme 3(c)), showing low conversion of **1** (1.4 %). This result indicates that the reactivity of alcohols is very low under these conditions, leading to high alcohol yields in hydrogenation of amides. Moreover, reaction of **2** was conducted with Ru/CeO$_2$ for 4 h (Scheme 3(d)). The conversion was very low (5.6%) compared with the case of cyclohexanecarboxamide (Table 1, entry 5), and the selectivity to methylcyclohexane was also very low (2.7%), suggesting that contribution of direct hydrogenolysis of C-N dissociation is low. Therefore, the reaction route (II) will be main over Ru/CeO$_2$ catalyst, which is similar to that proposed by homogeneous Ru complex catalyst[7d].

In conclusion, Ru/CeO$_2$ was an effective and reusable heterogeneous catalyst for selective hydrogenation of the C-N bond in amides with H$_2$ in water solvent under low reaction temperature of 333 K, and primary amides were transformed to the corresponding alcohols in high yields.



Scheme 2. Two possible reaction routes for reduction of amides to alcohols and amines.



Scheme 3. Hydrogenation of model substrates over Ru/CeO$_2$ catalyst. (a) **3**, (b) cyclohexanecarbaldehyde (**4**), (c) **1**, (d) **2**.

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