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Amination of Alcohols with Ammonia in Water over Rh–In Catalyst

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Amination of various C3 alcohols such as 1,2-propanediol with ammonia was catalyzed by Rh–In/C in water while Rh/C was totally inactive. Activated carbon FAC-10 was the best support in terms of activity and resistance to metal leaching. In the amination of 1,2-propanediol, Rh–In/C produced amino alcohols in 68% total selectivity and 38% conversion. XRD and TEM measurements showed that Rh–In alloy particle with size of 3–4 nm was formed on the carbon support.

Synthesis of primary amines is important because they are basic feedstock for polymers, dyes, pharmaceuticals, and agrochemicals.[1,2] The conventional method for the synthesis of primary amines is reductive amination of carbonyl compounds. However, this method requires the use of strong reducing reagents[3] or stoichiometric amount of hydrogen gas.[4] The amination of alcohols with ammonia ($ROH + NH_3 \rightarrow RNH_2 + H_2O$) has been intensively investigated as an attractive substitute method because the starting materials are inexpensive and readily available. This method produces H_2O as the only by-product and does not need stoichiometric amounts of hydrogen gas; therefore, it is an attractive solution in terms of green and atom-economical chemistry. Noble metals (Ru,[5–8] Ir,[9–11] Pt,[12] Cu,[13] and Os[14]), Co,[15,16] Ni,[17,18] and solid acid[19] catalysts are known to be effective in the amination of alcohol with ammonia. It is widely accepted that metal catalysts activate the alcohol by dehydrogenation to afford the corresponding carbonyl intermediate ($R^1R^2CHOH \rightarrow R^1R^2C{=}O + H_2$). This intermediate reacts with ammonia and elimination of water results in the formation of an imine ($R^1R^2C{=}O + NH_3 \rightarrow R^1R^2C{=}NH + H_2O$). Subsequent hydrogenation of imine produces the amine product ($R^1R^2C{=}NH + H_2 \rightarrow R^1R^2CHNH_2$).[20] However, most systems use gaseous or liquid ammonia that is highly toxic, corrosive, and explosive. Cheaper and easy-to-handle aqueous ammonia is a more attractive reagent. In recent years, amination of alcohols using aqueous ammonia and noble-metal catalysts has been investigated.[8–13] Water solvent is preferable from the viewpoint of green chemistry. However, when water is used as the main solvent, the presence of excess water may have an adverse effect on the position of the aldehyde–imine equilibrium, making amination of alcohols difficult.[21] For this reason, some of the catalytic systems used organic solvents such as mesitylene,[8,13] 1,4-dioxane, and methanol[12] as the main component of solvent. Only $[Cp^*Ir(NH_3)_3]I_2$[9] and a polymer-supported boron–iridium heterobimetallic catalyst[10] have been reported to be effective in amination of alcohols in water by using aqueous ammonia. The latter is the only heterogeneous system using water solvent.

In this study, we developed a stable supported metal catalyst for the amination of alcohols with ammonia in water. We chose Rh as an active metal because $[Rh(cod)Cl]_2$ complex is known to be an effective catalyst for the reductive amination of benzaldehyde in water.[22] We discovered that the combination of Rh and In is very effective.

Rh catalysts modified with various secondary metals were prepared by the coimpregnation method using activated carbon (Shirasagi FAC-10) support. In the following study, "C" as a support means Shirasagi FAC-10 unless noted otherwise. 1,2-Propanediol (1,2-PrD) was selected as a model substrate. The reaction was performed in a stainless steel autoclave with an inserted glass vessel. Methods for catalyst preparation, activity test, and product analysis are described in detail in the Supporting Information.[23] Table 1 shows the results of activity tests of catalysts with secondary metal/Rh = 1. Rh/C showed no activity (Entry 1). On the other hand, Rh–In/C catalyzed the reaction (Entry 2). Nearly equimolar amounts of 1-amino-2-propanol and 2-amino-1-propanol were formed with total initial selectivity of 89%. The main by-product was dimethylpiperazines formed by the condensation of two amino alcohol molecules. The activity of In/C was also very low (Entry 3).

Table 1. Amination of 1,2-PrD with ammonia over various supported metal catalysts[a]

Entry	Catalyst	Conversion/%	Selectivity/%			
			2-Amino-1-propanol	1-Amino-2-propanol	Dimethylpiperazines	Others
1	Rh/C	0.1	trace	trace	trace	trace
2	Rh–In/C	10.7	42	47	10	<1
3	In/C[b]	<0.1	—	—	—	—
4	Rh/C + In/C[c]	5.9	39	49	9	3
5	Rh–Ga/C	5.8	30	48	21	<1
6	Rh–Sn/C	1.5	32	32	35	<1
7	Rh–Zn/C	2.6	32	51	17	<1
8	Rh–Ge/C	<0.1	—	—	—	—
9	Rh–Bi/C	<0.1	—	—	—	—

[a]Reaction conditions: water 13.2 g, 1,2-PrD 0.76 g, NH_3 aq 6.08 g (total 20 mL), catalyst (Rh 5 wt %, secondary metal/Rh = 1) 50 mg, 453 K, H_2 5 MPa (at r.t.), 24 h. [b]In 5 wt %. [c]Rh/C 50 mg, In/C 50 mg.

Therefore, the activity of Rh–In/C was due to the synergy between Rh and In, as discussed later. In these tests, the reactor was filled with 5-MPa H_2 to maintain the metallic state of the catalyst, although this reaction does not stoichiometrically consume H_2. Decreasing the H_2 pressure decreased the selectivity toward amino alcohols and increased toward the by-products (Figure S1, Supporting Information). A physical mixture of Rh/C and In/C showed moderate activity, probably because of the interaction between Rh metal and eluted In species (Entry 4). Other additive metals were used for the amination of 1,2-PrD with aqueous ammonia. Although addition of Ga, Sn, and Zn afforded moderate activity, the promoting effect of these metals was smaller than that of In (Entries 5–7). Catalysts with Ge or Bi did not show the activity at all (Entries 8 and 9). To optimize the In loading amount, the effect of In/Rh molar ratio on the catalytic activity was investigated (Table S1). Even with small amount of In (In/Rh = 0.1 and 0.2), the catalysts had about half activity of the catalyst with In/Rh = 1. The catalytic activity became higher with larger amount of In in the range In/Rh = 0.2–1. The catalyst with In/Rh = 2 had almost the same activity as that with In/Rh = 1. The selectivity patterns were almost independent of In amount when In/Rh > 0.2. We used the catalyst with In/Rh = 1 in the following studies.

Recyclability of the Rh–In/C was examined (Figure S2, Supporting Information). Larger amount (50 → 200 mg) of catalyst was used to decrease the percentage of catalyst loss during the recovery process. The used catalyst was separated from the reaction solution by centrifugation. Then, the recovered wet catalyst was used for the next reaction without scale-down of the system. The reaction rate was almost maintained even after three-time uses.

We examined the dependence of the performance of Rh–In catalysts on various carbon supports (Table S3, Supporting Information). Carbon black (Vulcan XC-72) and three types of activated carbons (FAC-10, Carboraffin, and Shirasagi M) were tested as supporting materials. Rh–In supported on carbon black showed much lower activity than those supported on activated carbons (3.0% conv. versus 5.7–10.7%) and larger amount of metal elution (Rh 9.5% versus 0.9–5.6%). It suggests that it is difficult to stably keep the metal on the surface of carbon support in the reaction solution containing large amount of ammonia. The activity and amount of metal elution were changed with different activated carbon supports. Rh–In/FAC-10 showed the highest activity (10.7%) and small leaching amount of Rh and In (0.93% and 1.2%, respectively).

The time course of the amination of 1,2-PrD with aqueous ammonia catalyzed by Rh–In/C (In/Rh = 1) is shown in Figure 1. The initial total selectivity of amino alcohols was 94%. At longer reaction time, the selectivity to dimethylpiperazines increased and that to aminopropanols decreased. The yield of total amino alcohols was 26% at 38% conversion at 160 h.

We applied the amination system to various C3 alcohols to see the effects of the substrate structure (Table 2). The mono-ols, 1-propanol and 2-propanol, showed moderate reactivity (Entries 1 and 2). In the amination of 1-propanol, both the primary and secondary amines were produced (Entry 1). 2-Propanol showed higher conversion than 1-propanol (Entry 2). This is probably because the amination of 2-propanol proceeds through the ketone intermediate, which is more stable than the aldehyde one. Secondary diisopropylamine was not produced, probably because of the steric hindrance of isopropyl group. Rh–In/C catalyzed the amination of 1,2-PrD with the highest conversion (Entry 3). 1,3-Propanediol and glycerol, both of which have an OH group at the C3 position, showed low reactivity (Entries 4 and 5). In addition, most products had fewer functional groups than the substrate (propylamine and 1-propanol from 1,3-propanediol; propanols and aminopropanols from glycerol). These results indicated that hydrogenolysis of alcohols with OH groups at C1 and C3 positions proceeded over Rh–In/C. The reaction solution was basic; hence, the hydrogenolysis reaction might proceed through dehydrogenation, dehydration, and then hydrogenation, which mechanism has been proposed for the hydrogenolysis of glycerol to 1,2-PrD under basic conditions.[24]

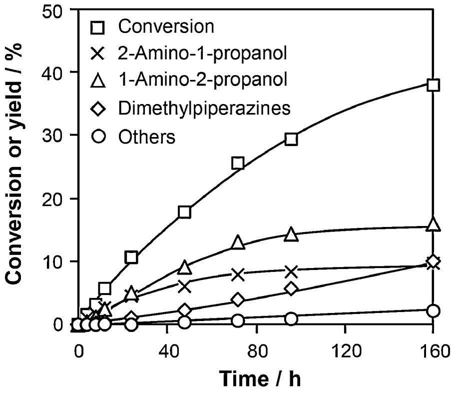

Figure 1. Time course of amination of 1,2-PrD over Rh–In/C. Reaction conditions: water 13.2 g, 1,2-PrD 0.76 g, NH_3 aq 6.08 g (total 20 mL), Rh–In/C (Rh 5 wt%, In/Rh = 1) 50 mg, 453 K, H_2 5 MPa (at r.t.), 4–160 h.

Table 2. Catalytic performances in the amination of various C3 alcohols with ammonia over Rh–In/C[a]

Entry	Reactant	Conv. /%	Product (selectivity/%)
1	1-Propanol	3.1	Propylamine (83), dipropylamine (17)
2	2-Propanol	6.0	Isopropylamine (>98)
3	1,2-PrD[b]	10.7	2-Amino-1-propanol (42), 1-amino-2-propanol (47), dimethylpiperazines (10), others (<1)
4	1,3-PrD[b]	1.9	1-Propanol (26), propylamine (64), others (9)
5	Glycerol	1.7	1-Propanol (5), 2-propanol (10), 2-amino-1-propanol (15), 1-amino-2-propanol (50), others (20)

[a]Reaction conditions: substrate 10 mmol, NH_3 0.1 mol, water balance (total 20 mL), Rh–In/C (Rh 5 wt%, In/Rh = 1) 50 mg, 453 K, H_2 5 MPa (at r.t.), 24 h. [b]PrD: propanediol.

We characterized the Rh–In/C catalyst with XRD, TEM, and XPS. Figure 2 shows the XRD pattern of Rh–In/C reduced with H_2. The pattern showed the peaks at $2\theta = 39.8$, 72.6, 57.8, and 86.0°, as well as the peak of carbon (ca. 20°). The peak positions were different from those due to fcc Rh metal ($2\theta = 41.08°$ for (111) reflection). These peaks suggested the

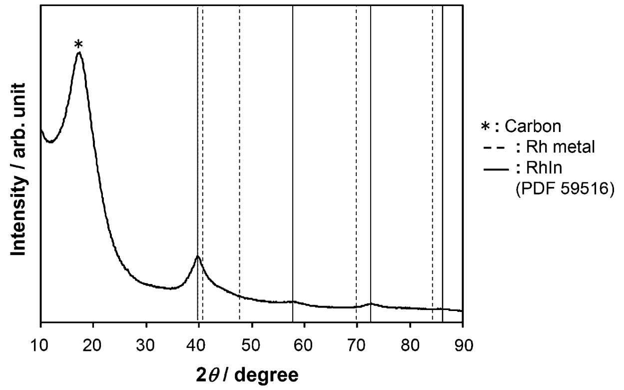

Figure 2. XRD pattern of reduced Rh–In/C (Rh 5 wt%, In/Rh = 1).

formation of Rh–In alloy (RhIn: PDF Ccode 59516). This alloy phase may be the active phase that induces the synergy in catalysis. In the TEM image of Rh–In/C (Figures S3 and S4, Supporting Information), particles with relatively narrow size distribution were observed. The average size ($\Sigma n_i d_i^3/\Sigma n_i d_i^2$; d_i: particle size, n_i: number of particle size with d_i) was calculated to be 4.2 nm. Rhodium 3d XPS of reduced Rh–In/C (Figure S5, Supporting Information) showed the peaks at 306.8 and 311.5 eV for $3d_{5/2}$ and $3d_{3/2}$, respectively. These values were similar to those of Rh^0 metal (307.2 and 311.9 eV), indicating that Rh was in the metallic state. Indium 3d XPS (Figure S6 and Table S4, Supporting Information) showed the peaks at 443.8 and 451.3 eV for $3d_{5/2}$ and $3d_{3/2}$, respectively, and small shoulders at 444.7 and 452.2 eV. The former peaks can be assigned to the In^0 state, and the latter ones to the In^{3+} state. The ratio of In^0 to In^{3+} was about 1.5. These data suggest that the Rh–In alloy phase is dominant on the catalyst.

Three steps (dehydrogenation, imine formation, and hydrogenation) are proposed to be involved in the amination. In the amination of (*S*)-(+)-1,2-PrD or (*R*)-(−)-1,2-PrD over Rh–In/C, optical isomer of remaining substrate was hardly racemized, suggesting that the rate-determining step was dehydrogenation (detailed results are described in Table S5, Supporting Information). We compared the activities of Rh/C and Rh–In/C in the dehydrogenation of 1,2-PrD under Ar (Table 3). Rh/C showed the dehydrogenation activity in the absence of amines (Entry 1); however, the activity was totally suppressed by the addition of secondary or tertiary amine (Entries 2 and 3). In the case of Rh–In/C, the dehydrogenation activity was higher than that of Rh/C in the absence of amines (Entry 4). Rh–In/C still showed some dehydrogenation activity in the presence of amines (Entries 5 and 6). The carbon balance was a little low, probably because of the successive reaction and the degradation. These results showed that the addition of In to Rh increases the resistance to the inhibition effect of amine/ammonia in the dehydrogenation of alcohols, which is the rate-determining step of amination of alcohols.

In conclusion, we demonstrated that the amination of alcohols such as 1,2-PrD with ammonia in the water solvent is catalyzed by Rh–In/C while Rh/C is totally inactive. Rh–In alloy particles with size of 3–4 nm was formed on the catalysts. Addition of In increases the activity of Rh in the dehydrogenation of alcohols, especially in the presence of amine or ammonia, while the dehydrogenation is the rate-determining step of the amination.

Table 3. Dehydrogenation of 1,2-PrD over Rh/C or Rh–In/C[a]

Entry	Catalyst	Added amine	Hydroxy acetone /mmol	C. B.[b] /%
1	Rh/C	—	0.23	100
2	Rh/C	$CH_3NH(n\text{-}C_3H_7)$	$<3.5 \times 10^{-3}$	101
3	Rh/C	$N(C_2H_5)_3$	$<3.5 \times 10^{-3}$	96
4	Rh–In/C	—	0.72	92
5	Rh–In/C	$CH_3NH(n\text{-}C_3H_7)$	0.18	81
6	Rh–In/C	$N(C_2H_5)_3$	0.22	87

[a]Reaction conditions: 1,2-PrD 10 mmol, amines 0 or 1 mmol, water balance (total 20 mL), Rh/C (Rh 5 wt%) or Rh–In/C (Rh 5 wt%, In/Rh = 1) 50 mg, 453 K, Ar 5 MPa (at r.t.), 24 h. [b]C. B.: Carbon balance.

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