Accepted Article

Title: One-step conversion of glutamic acid into 2-pyrrolidone on supported Ru catalyst in hydrogen atmosphere: remarkable effect of CO activation

Authors: Satoshi Suganuma, Akihiro Otani, Shota Joka, Hiroki Asako, Rika Takagi, Etsushi Tsuji, and Naonobu Katada

One-step conversion of glutamic acid into 2-pyrrolidone on supported Ru catalyst in hydrogen atmosphere: remarkable effect of CO activation

Satoshi Suganuma*[a], Akihiro Otani[a], Shota Joka[a], Hiroki Asako[a], Rika Takagi[a], Etsushi Tsuji[a], and Naonobu Katada[a]

Abstract: Glutamic acid, an abundant non-essential amino acid, was converted into 2-pyrrolidone in the presence of a Ru-supported catalyst under pressurized hydrogen atmosphere. This reaction pathway proceeded through the dehydration of glutamic acid into pyroglutamic acid, subsequent hydrogenation, and the dehydrogenation–decarbonylation of pyroglutaminol into 2-pyrrolidone. In the conversion of pyroglutaminol, Ru/Al$_2$O$_3$ exhibited extremely higher activity than Pt-, Pd-, and Rh-supported catalysts. Infrared (IR) analysis revealed that Ru can hydrogenate formed CO through dehydrogenation–decarbonylation of hydroxymethyl groups in pyroglutaminol, and also can easily desorb CH$_4$ from active sites on Ru. Furthermore, Ru/Al$_2$O$_3$ showed the highest catalytic activity among the tested catalysts in the conversion of pyroglutamic acid. Consequently, the conversion of glutamic acid produced a high yield of 2-pyrrolidone using the Ru-supported catalyst, which is the first report of the one-pot reaction under mild reaction conditions (433 K, 2 MPa H$_2$), in which instable amino acids above 473 K are undegradable.

1. Introduction

Biorefinery has attracted attention as an essential research subject because of the need for desirable alternative renewable resources to finite petroleum. Various biomass compounds are promising resources to be converted into essential chemicals through catalytic processes. Already oxygen-containing chemical intermediates have been produced from carbohydrates and fatty oils. In contrast, only few examples have been reported on the conversion of organic nitrogen-containing compounds, whose importance as intermediates of polymers, drugs, organic semiconductors, and dyes has been known.[1–5] Amino acids in proteins and their components are promising as feedstocks of amines, amides, and nitriles, which have conventionally been produced with insertion of nitrogen into petrochemical-originate compounds; typically, ammonia has been utilized for this purpose. The use of amino acids as the feedstocks will significantly reduce the energy consumption in the production of nitrogen-containing functional compounds.[6–9] Ammonia-based or -derived fertilizers are particularly used by the majority of modern agriculture, but the utilization efficiency of such fertilizers tends to be low. Thus it is significant to argue that this replacement of N-source is explicitly linked to energy savings. Glutamic acid is the most abundant amino acid in plant biomass. Bioethanol production from maize or wheat forms crude proteins in 20% dried distiller's grains, which are soluble in water and contain 20% L-glutamic acid.[10–13] The energy and resource demands for the extraction and purification of L-glutamic acid are not necessarily trivial. In addition, the U.S. Department of Energy has identified glutamic acid as one of the "Top 12" sugar-based chemical building blocks via biochemical or chemical conversions, where only two species of nitrogen-containing chemicals are included.[14] About 2 million tons of glutamic is produced by the fermentation from saccharides in a year. Thus, one can safely say that the nitrogen-containing compound which is most abundantly supplied at present is glutamic acid in plant biomass.

One amine and two carboxy groups in a molecular enable glutamic acid to have the potential for conversion into a wide range of compounds. An enzyme, glutamic acid α-decarboxylase, converts glutamic acid and its analogues into γ-aminobutylic acid, which is transformed into 2-pyrrolidone through a lactamization.[15] In addition, it was reported that succinonitrile and acrylonitrile were formed from the amino acid through multi-step reactions with homogeneous catalysts.[16,17] Heating glutamic acid over 393 K immediately produces pyroglutamic acid through dehydration–cyclization. Thus obtained pyroglutamic acid was transformed into chemical commodities in some previous reports.[18] Succinimide was synthesized from pyroglutamic acid through decarboxylation and oxidation using AgNO$_3$ as a catalyst and S$_2$O$_8^{2-}$ as an oxidant.[19] Also, hydrogenation of carboxyl groups in pyroglutamic acid produces pyroglutaminol, which can be converted into prolinol in an acidic solution under high temperature and pressured H$_2$.[20] Recently, it was found that 2-pyrrolidone was obtained through decarboxylation of pyroglutamic acid on Pd/Al$_2$O$_3$ in aqueous solution at 523 K and under inert atmosphere (N$_2$).[21] In this reaction, low pH improved the yield of 2-pyrrolidone from glutamic acid. Also, bio-based conversion of glutamic acid with decarboxylase produced γ-aminobutylic acid, which can be transformed into 2-pyrrolidone by intramolecular condensation at 473-513 K.[22,23]

2-Pyrrolidone has played important roles in the chemical industry. 2-Pyrrolidone is a convenient solvent with high boiling point and miscible with water and most of organic solvents. As a chemical platform compound, the ring-opening polymerization of five-membered lactam forms nylon 4, which is a biodegradable polymer.[24] Also, polyvinylpyrrolidone, a water-soluble polymer useful for solubilizer and dispersant, is synthesized from N-vinyl-2-pyrrolidone.[25] Various pharmaceutical medicines are also 2-pyrrolidone derivatives. Typically, 2-pyrrolidone is produced from γ-butyrolactone and NH$_3$, which are available from

[a]   Dr. S. Suganuma, A. Otani, S. Joka, H. Asako, R. Takagi, Dr. E. Tsuji, Prof. N. Katada
Center for Research on Green Sustainable Chemistry
Tottori University
4-101 Koyama-cho Minami, Tottori 680-8552, Japan
E-mail: suganuma@tottori-u.ac.jp

Supporting information for this article is given via a link at the end of the document.

petrochemical feedstocks. Very little research on the alternative bio-based process has been reported, as far as we know.[21-23]

Herein, we describe an approach used in producing 2-pyrrolidone from glutamic acid through hydrogenation of pyroglutamic acid into pyroglutaminol under high pressure of H_2 (Scheme 1). Usually, such supported noble metals as Pt/Al_2O_3 and Pd/Al_2O_3 are typically used as the catalysts for hydrogenation / dehydrogenation reactions. In a fact, Pd/Al_2O_3 has been reported to be an active catalyst for the decarboxylation of glutamic acid under inert atmosphere.[21] Therefore, Pt/Al_2O_3 and Pd/Al_2O_3 can be considered to be the benchmarks, and the catalytic activities of other supported metals are compared. Our working hypothesis was that pyroglutaminol was able to be converted into 2-pyrrolidone by eliminating hydroxymethyl groups. In this study, Ru/Al_2O_3 showed a remarkably high yield of 2-pyrrolidone in pyroglutaminol conversion. IR analysis reveals the reason for the higher activity of Ru/Al_2O_3 than Pt-, Pd-, or Rh-loaded catalysts. More importantly, the formation of 2-pyrrolidone from glutamic acid or pyroglutamic acid firstly achieved a high yield under milder reaction conditions in H_2 atmosphere than the other conversion of glutamic acid, in which instable amino acids above 473 K are decomposed.
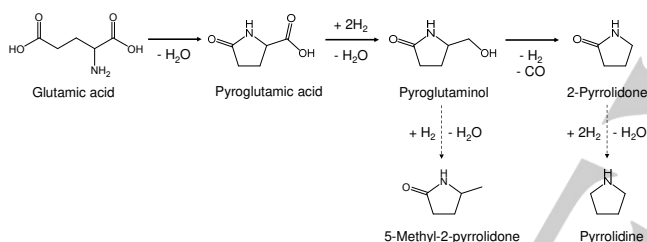
Scheme 1. Reaction pathway for the formation of 2-pyrrolidone from glutamic acid and side reactions.

2. Results

2.1. Structure of catalyst

Figure 1 shows the XRD patterns of prepared noble metal catalysts. Intact peaks observed on all the catalysts indicate γ-Al_2O_3 as a support. Marked peaks showed metal species of the elements with a diameter of < 10 nm. The valence state of the surface on the catalysts was investigated using XPS (Figure 2). Ru $3p_{3/2}$ spectrum (a) of Ru/Al_2O_3 shows the only peak at 461.7 eV assigned to Ru (oxidation state: 0, as metal).[26] Similarly, the peak at 314.5 eV in Pt $3d_{3/2}$ spectrum (c) of Pt/Al_2O_3 was attributed to Pt metal.[27] The surface Ru and Pt on the catalysts were completely reduced into metal. Spectrum of Pd in the region of $3d_{5/2}$ and $3d_{3/2}$ on Pd/Al_2O_3 (b) were composed of intense doublet peaks at 334.3 and 339.5 eV and weak doublet peaks at 335.6 and 341.0 eV, which were assigned to Pd metal and Pd^{2+} in PdO, respectively.[28] In the spectrum of Rh in the similar energy level to Pd, two types of doublet peaks was attributed to Rh metal (307.1 and 311.8 eV) and Rh^{3+} in Rh_2O_3 (309.2 and 313.9 eV).[29] Pd and Rh metals existed with small amount of oxides.

The TEM (Figure 3) indicated that the particle size of all noble metals had a narrow distribution, but slightly wide distribution of Pd. The average particle diameters was 2.8–3.5 nm, and the order was Rh < Pt < Pd < Ru. The noble metals were uniformly dispersed on the support, being consistent with the XRD results. The amount of CO chemisorbed on Rh was more than 3 times of those on the other catalysts (Table 1). The average particle diameters of metals were calculated from the CO chemisorption. The order was Rh < Pt < Ru < Pd, indicating dissimilar dimensions observed by TEM due to including coarse particles on Pd/Al_2O_3.
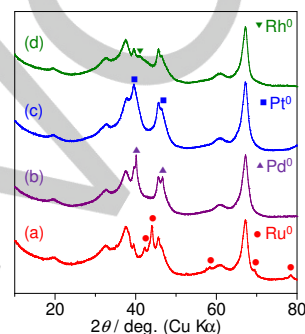
Figure 1. XRD patterns for (a) Ru/Al_2O_3, (b) Pd/Al_2O_3, (c) Pt/Al_2O_3, and (d) Rh/Al_2O_3.
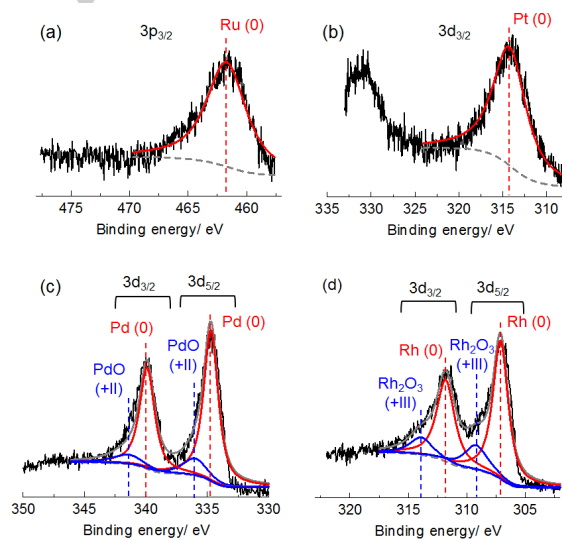
Figure 2. XPS spectra of (a) Ru $3p_{3/2}$ region in the Ru catalyst, (b) Pt $3d_{5/2}$ region in the Pt catalyst, (c) Pd $3d_{5/2}$ and $3d_{3/2}$ region in the Pd catalyst, and (d) Rh $3d_{5/2}$ and $3d_{3/2}$ region in the Rh catalyst.
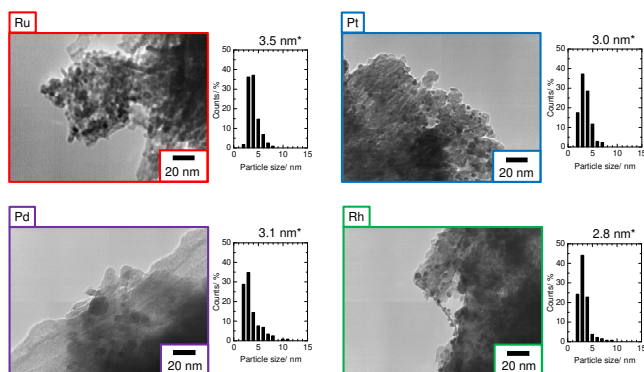
Figure 3. TEM images and particle size distributions of Al_2O_3-supported noble metal catalysts. * displays average particle diameter.

Table 1. CO chemisorption results on the noble metal catalysts.

Metal (M)	Chemisorbed amount / mmol g^{-1}	Metal dispersion /%	Average particle diameter/ nm
Pt	0.058	22.8 [a]	5.0 [a]
Rh	0.208	42.9 [a]	2.6 [a]
Pd	0.072	15.2 [a]	7.4 [a]
Ru	0.068	23.1 [b]	5.7 [b]

[a] The stoichiometry was assumed as CO/M = 1. [b] The stoichiometry was assumed as CO/Ru = 0.6.

2.2. Conversion of pyroglutaminol and pyroglutamic acid on the noble metal catalysts

2.2.1. Conversion of pyroglutaminol into 2-pyrrolidone

Figure 4 compares the yield of products on the supported noble metal catalysts at 433 K for 1 h in 1 MPa of two different atmospheres, i.e., (a) N_2 and (b) H_2. In N_2, all the employed catalysts showed negligible yields of products including the desired one, i.e., 2-pyrrolidone, and potential byproduct of assumed sequential reaction (Scheme 1), i.e., pyrrolidine. In H_2, Ru/Al_2O_3 exhibited extremely high activity for the formation of 2-pyrrolidone, while all the other catalysts had little activity. Time courses on Ru/Al_2O_3 (Figure S1) revealed that pyroglutaminol was virtually converted into 2-pyrrolidone from 10 minutes, and intermediate was not detected. Not only the apparent activity as above, but also the turnover frequency (TOF) was also high on Ru/Al_2O_3 in 1 MPa H_2, as shown in Table 2. It is noteworthy that TOF on Ru/Al_2O_3 in H_2 was more than 200 times larger than those on the other noble metal catalysts. On Ru/Al_2O_3, such by-products as pyrrolidine and 5-methyl-2-pyrrolidone, predicted as Scheme 1, were not significantly observed in the liquid products. As shown in Figure S2, the analysis of gaseous compounds in the reactor after the reaction on Ru/Al_2O_3 in 1 MPa H_2 at 433 K

for 1 h detected intensely H_2 and CH_4 with the air components (O_2 and N_2) contaminated during the gas sampling, whereas CO (retention time: 0.49 and 7.75 min) and CO_2 (1.23 min), were not detected at all.

In summary, the elimination of hydroxymethyl group from pyroglutaminol yielding 2-pyrrolidone was found to proceed in the pressurized H_2 on Ru/Al_2O_3, but not in N_2 nor on the other noble metal catalysts. Although the reaction formula (-CH_2OH → -H + CH_2O) indicates the formation of CO and H_2 or some oxygen-containing compounds, CH_4 was mainly found in the gaseous products.
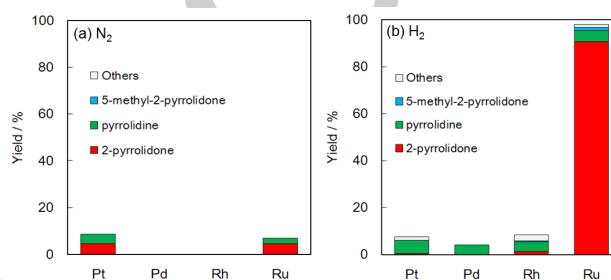

Figure 4. Yield of products in the conversion of pyroglutaminol using supported metal catalysts in atmosphere of (a) N_2 and (b) H_2. Reaction conditions: 26 mmol L^{-1} of pyroglutaminol aq. 50 mL, catalyst 0.2 g, initial pressure 1 MPa, 433 K, 1 h.

Table 2. Kinetic parameters of the noble metal catalysts.

Metal (M)	Reaction rate [a] / mmol g-cat^{-1} h^{-1}	TOF [b] / h^{-1}
Pt	0.03	0.4
Rh	0.08	0.4
Pd	0	0
Ru	5.89	86.6

[a] Rate for 2-pyrrolidone formation. [b] Turnover frequency (TOF) values were calculated by dividing the rate for 2-pyrrolidone formation by the amount of chemisorbed CO on the catalysts as shown in Table 1.

2.2.2. IR measurements of species on the catalysts formed from pyroglutaminol

After the adsorption of pyroglutaminol at a low temperature, the thermal behavior of the adsorbed species in Ar or H_2(6%)/Ar flow was investigated with *in-situ* IR, as shown in Figure S3. On all the employed noble metal catalysts in both atmosphere, the bands due to stretching of O–H in hydroxymethyl groups (around 3500 cm^{-1}), stretching of N–H in amide groups (around 3050 cm^{-1}), stretching of C=O in amide groups (1570 cm^{-1}), and bending of CH_2 in intact and transformed pyroglutaminol molecules (1460 cm^{-1}) were observed; it is possible that these

bands overlap the bending bands of N–H (1490-1580 cm^{-1}).[30] In addition, weak bands due to plane bending of O–H coupled with wagging of adjacent CH_2 in intact pyroglutaminol molecules (1420 and 1330 cm^{-1}) and stretching of C=O in aldehyde groups formed from hydroxymethyl groups (1670 cm^{-1}) were observed.

Besides the above bands commonly observed, a characteristic absorption was found at 1800–2300 cm^{-1}, as enlarged in Figure 5, and assignments were carried out according to literature (Figure S4).[31 −35] The adsorbed species itself, and its change in absorbance by varying the temperature / atmosphere were dependent on the noble metal element, as follows.

On Ru/Al$_2$O$_3$ in Ar (Figure 5 (a)), bridge-type CO adsorbed on Ru [31] was found at 1850 cm^{-1}. However, it was observed that this species desorbed above 373 K in H$_2$/Ar (Figure 5 (b)); besides, CO linearly adsorbed on isolated Ru [31,32] was found at 1973 cm^{-1} at 423 K but desorbed above 473 K. On Rh/Al$_2$O$_3$ in Ar (Figure 5 (c)) and H$_2$/Ar (Figure 5 (d)), no band was observed in the enlarged spectra. On Pt/Al$_2$O$_3$ in Ar (Figure 5 (e)), CO linearly adsorbed on Pt^0 was observed at 2055 cm^{-1},[33] and this band increased with temperature. In H$_2$/Ar (Figure 5 (f)), CO linearly adsorbed on Pt carbonyl hydride were found at 1990–2020 cm^{-1}.[34,35] On Pd/Al$_2$O$_3$ in Ar (Figure 5 (g)), bridge-type CO adsorbed on Pd [34] was found at 1896 cm^{-1} above 473 K. However, this weak band was not observed in H$_2$/Ar (Figure 5 (h)).
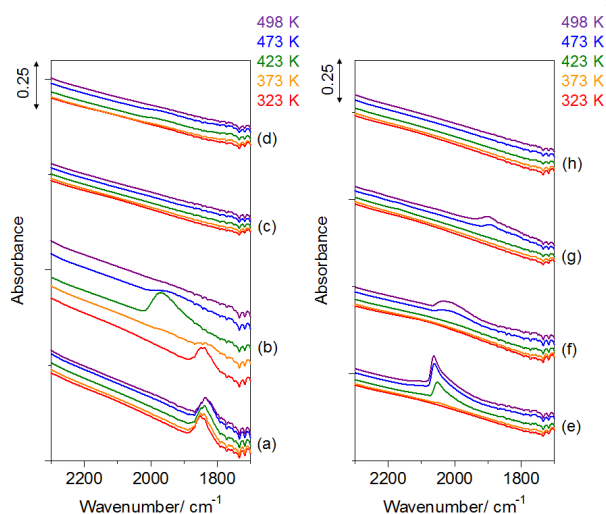
Figure 5. Enlarged IR spectra of adsorbed species, formed from pyroglutaminol, on the catalysts ((a) and (b) Ru/Al$_2$O$_3$, (c) and (d) Rh/Al$_2$O$_3$, (e) and (f) Pt/Al$_2$O$_3$, and (g) and (h) Pd/Al$_2$O$_3$) during the ramping process in the flow of Ar ((a), (c), (e), and (g)) or H$_2$ (6 vol%)/Ar ((b), (d), (f), and (h)).

2.2.3. Conversion of pyroglutamic acid to 2-pyrrolidone

Reaction of pyroglutamic acid was examined at 433 K for 2 h in 2 MPa of H$_2$ (Figure 6). Apparently high yield of 2-pyrrolidone was found on Ru/Al$_2$O$_3$. Pyroglutaminol, an intermediate on the pathway from pyroglutamic acid to 2-pyrrolidone as evidenced in the following section, was also observed, but the yields of such

by-products as 5-methyl-2-pyrrolidone and pyrrolidine were small. On the contrary, Pt, Pd, and Rh loaded on Al$_2$O$_3$ formed pyroglutaminol as a main product. This is in agreement with a literature reporting that the decarboxylation of pyroglutamic acid into 2-pyrrolidone and carbon dioxide on Pd/Al$_2$O$_3$ in N$_2$ did not proceed below 448 K, although it was observed at 523 K.[21] In a fact, in the present reaction conditions (433 K), the decarboxylation did not occur, but only hydrogenation of pyroglutamic acid proceeded. Rh/Al$_2$O$_3$ showed a higher yield of 2-pyrrolidone than Pt- and Pd-loaded catalysts, but yields of 2-pyrrolidone over all of these catalysts were obviously lower than that on Ru/Al$_2$O$_3$.
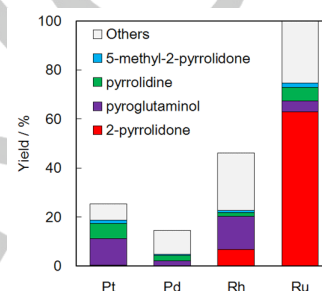
Figure 6. Yield of products in the conversion of pyroglutamic acid using the metal catalysts under pressurized H$_2$. Reaction conditions: 26 mmol L^{-1} of pyroglutamic acid aq. 50 mL, catalyst 0.2 g, initial pressure 2 MPa, 433 K, 2 h.

2.3. Effect of reaction conditions on conversion of pyroglutamic acid over Ru catalyst

Hereafter, the influence of the reaction conditions on the catalytic activity in this section was evaluated using Ru/Al$_2$O$_3$.

Figure 7 shows the conversion and selectivity of the products on Ru/Al$_2$O$_3$ as functions of reaction time in the transformation of pyroglutamic acid. Pyroglutaminol was mainly formed for the first 0.5 h, and then, its selectivity decreased while 2-pyrrolidone increased up to 2 h, indicating that pyroglutaminol was an intermediate between pyroglutamic acid and 2-pyrrolidone, as postulated in Scheme 1. At >2 h, pyrrolidine was found to increase with decrease of 2-pyrrolidone, suggesting that pyrrolidine was formed from 2-pyrrolidone via consequent reaction (as drawn in Scheme 1) with keeping the low yield of such a parallel product as 5-methyl-2-pyrrolidone.

Figure 8 showed the influence of reaction temperatures. At 393 K, the conversion was moderate, and pyroglutaminol as a main product and a small amount of 2-pyrrolidone were formed. Rising the temperature up to 433 K increased the selectivity of 2-pyrrolidone with decreasing the pyroglutaminol selectivity, supporting that pyroglutaminol was the intermediate, and 2-pyrrolidone was formed via pyroglutaminol. Other products, such as 5-methyl-2-pyrrolidone and pyrrolidine, were hardly formed. Too high temperatures >433 K thoroughly decreased 2-pyrrolidone and increased selectivity of pyrrolidine and other products.
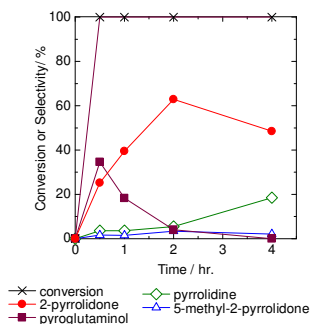
Figure 7. Time courses of the conversion and yield of the products in the transformation of pyroglutamic acid. Reaction conditions: 26 mmol L^{-1} of pyroglutamic acid aq. 50 mL, Ru/Al$_2$O$_3$ 0.2 g, initial pressure 2 MPa of H$_2$, 433 K.
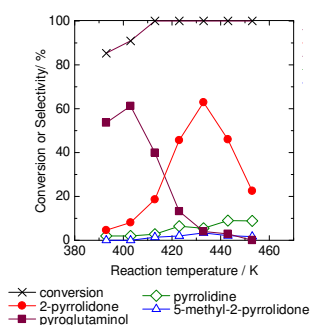

Figure 8. Influence of reaction temperature on the conversion and selectivity of the products in the transformation of pyroglutamic acid. Reaction conditions: 26 mmol L^{-1} of pyroglutamic acid aq. 50 mL, Ru/Al$_2$O$_3$ 0.2 g, initial pressure 2 MPa of H$_2$, 2 h.

Figure 9 showed the influence of H$_2$ pressure on the catalytic activities at 433 K for 2 h. As stated before, the reaction did not proceed without H$_2$. Introduction of H$_2$ up to 2 MPa generated the reactivity. Pyroglutaminol was the main product at 0.5 MPa. It is noteworthy that the material balance was low in these conditions, and it is presumed that the materials were adsorbed on the surface of catalyst. The pressure of H$_2$ increased 2-pyrrolidone selectivity. However, the excess high pressure resulted in the low selectivity of 2-pyrrolidone and high selectivity of pyrrolidine. Similarly to the elongation of reaction time and elevation of the reaction temperature, elevation of the H$_2$ pressure was thus observed to enhance the extent of reaction.

The reusability of Ru/Al$_2$O$_3$ was tested as shown in Figure 10. After each reaction run, the catalyst was washed thoroughly with water to remove the organic compounds from the surface, and it

was reused for subsequent reaction run. No decrease in activity was displayed by the reaction continuing for five runs, showing the stability of Ru/Al$_2$O$_3$.
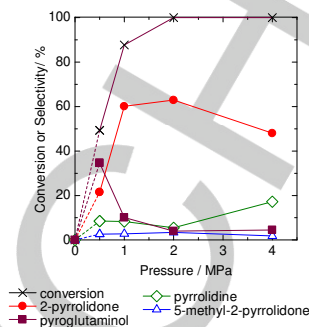

Figure 9. Influence of initial H$_2$ pressure on the conversion and yield of the products in the transformation of pyroglutamic acid. Reaction conditions: 26 mmol L^{-1} of pyroglutamic acid aq. 50 mL, Ru/Al$_2$O$_3$ 0.2 g, 433 K, 2 h.
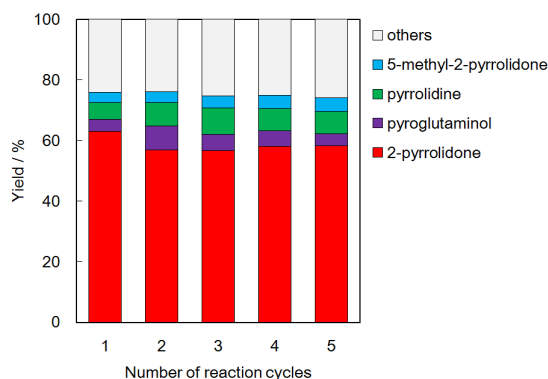
Figure 10. Reusability tests of Ru/Al$_2$O$_3$. Reaction conditions: 26 mmol L^{-1} of pyroglutamic acid aq. 50 mL, catalyst 0.2 g, initial pressure 2 MPa of H$_2$, 433 K, 2 h.

2.4. Conversion of glutamic acid on Ru/Al$_2$O$_3$

The catalytic activity was shown for the conversion of glutamic acid as in Figure 11. 2-Pyrrolidone yield was still high in this reaction, which was comparable with that in the conversion of pyroglutamic acid. No significant influence due to the difference of reactants between glutamic acid and pyroglutamic acid was observed.

Figure 11. Yield of products in the conversion of (a) pyroglutamic acid and (b) glutamic acid. Reaction conditions: 26 mmol L^{-1} of reactant solution 50 mL, Ru/Al$_2$O$_3$ 0.2 g, initial pressure 2 MPa of H$_2$, 433 K, 2 h.

3. Discussion

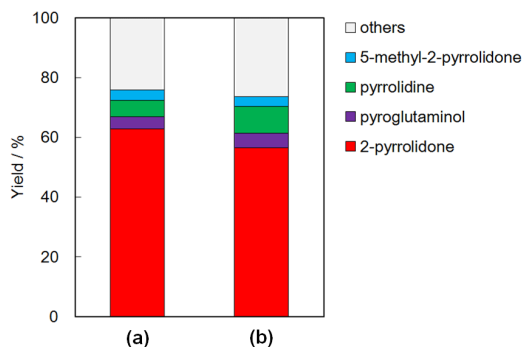In the previous chapter, it has been shown that the reaction of pyroglutamic acid into pyroglutaminol proceeded on various noble metals; more exactly, the activity of Pt and Rh for this step seemed higher than that of Pd. However, the next step from pyroglutaminol into 2-pyrrolidone seems a difficult reaction and hence did not proceed on most catalysts in both cases where the reactant was pyroglutamic acid, and pyroglutaminol was supplied as the reactant. Only on Ru/Al$_2$O$_3$, the elimination of hydroxymethyl group from pyroglutaminol, forming 2-pyrrolidone, was smoothly catalyzed without distinct side reactions. It is important to note that the reaction was eliminating CO and H$_2$ from the chemical formula, but the introduction of H$_2$ generated and enhanced the activity on Ru/Al$_2$O$_3$. Probably, the undetectable other product in the reaction of pyroglutamic acid was formed by intermolecularly linking between pyroglutamic acid and products, and adsorbed on Ru/Al$_2$O$_3$.

After the contact of pyroglutaminol, the *in-situ* IR analysis indicated that linear CO was adsorbed on Pt. CO adsorption experiments indicated the larger chemisorption capacity of CO on Rh/Al$_2$O$_3$ than Pt/Al$_2$O$_3$, but in the *in-situ* IR demonstrated that the formation of CO was more significant on Pt/Al$_2$O$_3$. Besides, Pd/Al$_2$O$_3$, which were not found to be active for the reaction of pyroglutaminol, slightly show the adsorbed CO in the *in-situ* IR. It is suggested that the decarbonylation of pyroglutaminol to form CO proceeded on Pt, but the formed CO was strongly adsorbed on these metals to prohibit successive reaction, because the adsorption of CO on such noble metals as Pt is often too strong to prohibit the catalytic activities of these metals. [31,36,37] It is reasonably explained that the intensity of adsorbed CO in the IR spectrum was much larger on Pt than Rh, against the order of CO adsorption capacity, because the ability of Pt for decarbonylation of pyroglutaminol was higher than that of Rh, and in addition, Pd with no activity in pyroglutaminol conversion hardly forms CO.

On the other hand, the bridge-type CO was formed on Ru/Al$_2$O$_3$ in an inert atmosphere. Introduction of H$_2$ diminished the bridge-type CO and made the linear-type CO formed and then desorbed; besides, formation of CH$_4$ was found in H$_2$. The

introduction of H$_2$ simultaneously generated the catalytic activity in pyroglutaminol conversion into 2-pyrrolidone on Ru. It has been known that the bridge-type CO was more active than the linear-type CO,[31] and Ru had higher catalytic activity than Rh, Pt, and Pd for CO–H$_2$ reaction.[36-38] Therefore, the reason for the high activity of Ru/Al$_2$O$_3$ in H$_2$ for the desired reaction should be that the dehydrogenation and decarbonylation from pyroglutaminol formed the bridge-type CO on Ru, and the Ru species catalyzed the hydrogenation of CO into CH$_4$ which was readily desorbed from the surface to regenerate the active site.

Similar mechanism have been reported in reactions such as tetrahydrofurfuryl alcohol to tetrahydrofuran, L-valine to isobutylamine, and levulinic acid to 2-butanol.[39–42] These reactions were reported to form CH$_4$ from CO, just like the reaction in our research.

According to the IR measurements and pyroglutaminol conversion tests, a possible reaction pathway is hypothesized as Scheme 2. Pyroglutaminol was converted into 5-oxoprolinal through dehydrogenation. 5-Oxoprolinal, however, was reactive for decarbonylation, and have a short lifetime making impossible to detect in the analysis of reaction solution. Then, 2-pyrrolidone and CO were formed. CO on Ru was then rapidly hydrogenated into CH$_4$. In the conversion of pyroglutaminol, Ru/Al$_2$O$_3$ adsorbed the CO molecules with the bridge structure, catalyzed the hydrogenation of CO into CH$_4$, and recovered the active sites after desorption of CH$_4$. In contrast, Pt adsorbed CO with the linear state, and Pd and Rh did not catalyze even the decarbonylation. It was previously reported that the adsorption energy of CO on metals is stronger than that of H$_2$,[43,44] and CO hydrogenation needs the dissociation of CO.[45] Therefore, the linear-type CO adsorbed on Pt was less active for the hydrogenation into CH$_4$ than bridge-type CO adsorbed on Ru. Consequently, the CO adsorbed on Pt remained poisoning the active sites in pyroglutaminol conversion. In summary, Ru/Al$_2$O$_3$ smoothly catalyzed the carbonylation of 5-oxoprolinal, and the adsorbed CO on Ru was much more active in the hydrogenation than that on the other catalysts. Therefore, the Ru catalyst without poisoning exhibited higher activity in pyroglutaminol conversion.
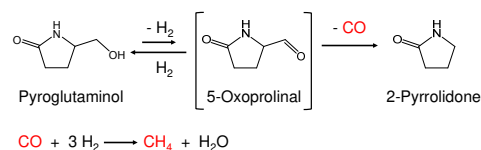
Scheme 2. Reaction pathway in pyroglutaminol conversion.

Also for the conversion of pyroglutamic acid, Ru/Al$_2$O$_3$ exhibited a far higher yield of 2-pyrrolidone than the other catalysts. Probably, Pt, Pd, and Rh were difficult to catalyze the hydrogenation of pyroglutamic acid, and/or poisoned by the formed CO in the step of pyroglutaminol conversion into 2-pyrrolidone. CO and the carbonyl groups in 5-oxoprolinal and pyroglutamic acid are considered to be less reactive on Pt, Pd, and Rh. Therefore, the catalysts were inactive. XPS profiles of

Rh and Pd indicated the oxides remaining in these catalysts, and the possibility that the oxides deteriorated active site on these catalysts cannot be ruled out. In contrast, the hydrogenation of pyroglutamic acid over Ru/Al$_2$O$_3$ smoothly proceeded, and the active sites were not poisoned by CO. Therefore, the 2-pyrrolidone productivity on Ru in the conversion of pyroglutamic acid was superior to those of Pt-, Pd-, and Rh-loaded catalysts, as found in the direct reaction of pyroglutaminol. The proposed reaction pathway is highly related to the decarbonylation and CO hydrogenation, compared with hydrogenation and dehydrogenation.

Ru/Al$_2$O$_3$ exhibited 60% of 2-pyrrolidone yield under appropriate reaction conditions for 2 h at 433 K in 2 MPa of H$_2$, and stable activity after five runs. Also, glutamic acid was converted into 2-pyrrolidone on Ru/Al$_2$O$_3$, just like pyroglutamic acid. The results suggested that the dehydration of glutamic acid into pyroglutamic acid occurred at a high reaction rate, and thus the difference between the reactants did not influence the yield of 2-pyrrolidone.

Up to this stage, the maximum yield of 2-pyrrolidone was about 60% in the conversion of glutamic acid. Therefore, the yield should be improved. We have shortly investigated the influence of support of Ru catalyst on the activity. In some cases, the activity was enhanced, but the reason has not been clarified. It is speculated that the support influenced the electronic state of Ru or adsorbed state of the reactants on the surface. In a future work, the effects of supports and Ru loading will be studied to improve 2-pyrrolidone productivity.

4. Conclusions

Efficient one-pot conversion of glutamic acid, which is one of the abundant nitrogen-containing compounds, into 2-pyrrolidone can be realized by Ru-supported catalyst under pressurized H$_2$. We studied the reactions using pyroglutaminol, pyroglutamic acid, and glutamic acid as reactants. In the conversion of pyroglutaminol, Ru/Al$_2$O$_3$ exhibited an extremely higher activity than Pt-, Pd-, and Rh-supported catalysts. IR measurement of adsorbed species formed from pyroglutaminol on the catalysts with heating has revealed that CO was formed from pyroglutaminol, and Ru rapidly converted it into CH$_4$. As a result, the active sites on Ru were highly feasible in the conversion of pyroglutaminol. The conversion of pyroglutamic acid was also effectively catalyzed by Ru catalyst compared with other tested catalysts. The durability of Ru catalyst after five runs was exhibited. In the conversion of glutamic acid, Ru/Al$_2$O$_3$ showed high yield of 2-pyrrolidone comparable to the case of conversion of pyroglutamic acid. The characteristics of Ru/Al$_2$O$_3$ are beneficial to the conversion of various amino acids into valuable nitrogen-containing chemicals through one-pot conversion under mild reaction conditions, in which even instable amino acids above 473 K are undegradable.

Experimental Section

Preparation of supported noble metal catalysts

Noble metal catalysts loaded on Al$_2$O$_3$ (metal lading: 5 wt%) were purchased from FUJIFILM Wako Pure Chemical Corporation. The catalysts were treated at 673 K for 3 h in H$_2$ flow to obtain Ru/Al$_2$O$_3$, Pt/Al$_2$O$_3$, Rh/Al$_2$O$_3$, and Pd/Al$_2$O$_3$; this step is essential to stabilize the noble metals before reactions under high pressure hydrogen atmosphere.

Physicochemical characterization

The crystalline phases of the catalysts were analyzed by X-ray diffraction (XRD, Rigaku Ultima IV diffractometer) with Cu Kα radiation in the 2θ range from 10° to 80°. X-ray photoelectron spectroscopy (XPS, ULVAC-PHI PHI5000 VersaProbe II) was operated with Al Kα radiation (1486.6 eV). Charging effects on the Ru, Pd, and Rh catalysts were corrected using the Al 2p peak (74.6 eV) of the Al$_2$O$_3$ support, while that on the Pt catalyst was corrected using the Al 2s peak (119.5 eV).[46] Transmission electron microscopy (TEM, JEOL JEM1400 Plus) was applied at an acceleration voltage of 80.0 kV. Samples were dispersed on copper grids using ethanol after ultrasonic pretreatment. The amounts of CO chemisorbed on the catalysts were recorded at 323 K from 0.01 to 50 kPa using a volumetric adsorption apparatus (MicrotracBel BELSORP-max). Prior to gas adsorption, the samples were heated at 573 K in O$_2$ and then H$_2$ flow, and evacuated with cooling to 323 K.

Catalytic reactions

Catalytic activities for the reaction of pyroglutaminol [(S)-5-(Hydroxymethyl)-2-pyrrolidinone, Tokyo Chemical Industry], L-pyroglutamic acid (Tokyo Chemical Industry), and L-glutamic acid (FUJIFILM Wako Pure Chemical Corporation) were measured using the reactants as received. In a typical reaction run, an aqueous solution of a reactant (0.026 mol L^{-1}, 50 mL) and a catalyst (0.2 g) were charged into a batch autoclave reactor (120 mL, Taiatsu Techno). After sealing, the interior atmosphere was purged and pressurized to the desired pressure using H$_2$ or N$_2$. The solution was stirred at 500 rpm and heated at the desired reaction temperature. After the reaction, the autoclave was cooled to room temperature. The catalyst was separated from the solution by centrifugation. The resulting solution, mixed with tetraethylene glycol dimethyl ether (Tokyo Chemical Industry) as an internal standard, was analyzed using a gas chromatograph (GC-2014, Shimadzu) with a capillary column (HP-INNOWax) and a flame ionization detector (FID). The interior gas in an autoclave reactor was collected in a sampling bag made from aluminum and analyzed by a GC (GC-2014, Shimadzu) equipped with parallel branched columns of activated carbon and molecular sieve (WG-100), and thermal conductivity detectors (TCD).

Conversion was calculated in the following expression. ([Conversion (%)] = (1- [a detected reactant (mol)] / [a charged reactant (mol)]) •100)

Yield of a product was calculated in the following expression. ([Yield (%)] = [a detected product (mol)] / [a charged reactant (mol)]) •100)

Others indicated undetected products by GC, and yield of others was calculated from the expression: ([conversion (%)] − [total yield of detected products (%)]).

The initial reaction rates for 2-pyrrolidone formation on the catalysts were calculated through the amount of formed 2-pyrrolidone for first 1 h divided by the weight of catalyst. The turnover frequency (TOF) was calculated by normalizing the initial rate for 2-pyrrolidone formation with the number of accessible metal atoms which was determined by the CO adsorption.

The durability of the Ru/Al$_2$O$_3$ catalyst was examined in five consecutive batch runs for the catalytic conversion of pyroglutamic acid at 433 K in 2 MPa H$_2$ for 2 h. After a reaction run, the used catalyst was centrifuged and washed using 50 mL of deionized water for three times. The thus recovered catalyst was dried at 383 K for 12 h and put into a new reactant mixture for the next run.

IR measurements of species formed from pyroglutaminol on catalysts

A metal-loaded catalyst (0.2 g) was immersed in an aqueous solution of pyroglutaminol (0.026 mol L^{-1}, 50 mL) and stirred for 1 h at room temperature. After this step for adsorption of pyroglutaminol, the solid was separated from the resulting solution by filtration and washed using deionized water for three times, before it was finally dried at 383 K overnight. The IR analysis of species adsorbed on catalyst samples was carried out using an IR spectrometer (FT/IR-4200, JASCO). The catalyst powder was compressed at 20 MPa into a self-supporting disk having a diameter of 1 cm and then set in the *in-situ* IR cell (MicrotracBel IRMS-TPD). The spectra were recorded in Ar or H$_2$(6%)/Ar flow (50 mL min^{-1}) with heating the sample at a ramp rate of 2 K min^{-1} up to 498 K at 4.1 kPa.

Acknowledgements

[1]   S. E. Davis, M. S. Ide, R. J. Davis, *Green Chem.* **2013**, *15*, 17-45.
[2]   H. Kobayashi, A. Fukuoka, *Green Chem.* **2013**, *15*, 1740-1763.
[3]   M. Besson, P. Gallezot, C. Pinel, *Chem. Rev.* **2014**, *114*, 1827-1870.
[4]   M. J. Gilkey, B. Xu, *ACS Catal.* **2016**, *6*, 1420-1436.
[5]   X. Li, P. Jia, T. Wang, *ACS Catal.* **2016**, *6*, 7621-7640.
[6]   J. Sanders, E. Scott, R. Weusthuis, H. Mooibroek, *Macromol. Biosci.* **2007**, *7*, 105-117.
[7]   E. Scott, F. Peter, J. Sanders, *Appl. Microbiol. Biotechnol.* **2007**, *75*, 751-762.
[8]   L. Claes, R. Matthessen, I. Rombouts, I. Stassen, T. D. Baerdemaeker, D. Depla, J. A. Delcour, B. Lagrain, D. E. De Vos, *ChemSusChem* **2015**, *8*, 345-352.
[9]   M. Tamura, R. Tamura, Y. Takeda, Y. Nakagawa, K. Tomishige, *Chem. Eur. J.* **2015**, *21*, 3097-3107.
[10]   M. J. Spiehs, M. H. Whitney, G. C. Shurson, *J. Anim. Sci.* **2002**, *80*, 2639-2645.
[11]   R. L. Belyea, K. D. Rausch, M. E. Tumbleson, *Bioresour. Technol.* **2004**, *94*, 293-298.
[12]   Y. Kim, N. S. Mosier, R. Hendrickson, T. Ezeji, H. Blaschek, B. Dien, M. Cotta, B. Dale, M. R. Ladisch, *Bioresour. Technol.* **2008**, *99*, 5165-5176.
[13]   T. M. Lammens, M. C. R. Franssen, E. L. Scott, J. P. M. Sanders, *Biomass Bioenergy* **2012**, *44*, 168-181.

[14]   Committee on Grand Challenges for Sustainability in the Chemical Industry, National Research Council. In *Sustainability in the Chemical Industry: Grand Challenges and Research Needs*, 1st ed.; National Academies Press: Washington, D.C.; Chapter 3, p. 41-53.
[15]   T. M. Lammens, D. D. Biase, M. C. R. Franssen, E. L. Scott, J. P. M. Sanders, *Green Chem.* **2009**, *11*, 1562-1567.
[16]   T. M. Lammens, J. Le Nôtre, M. C. R. Franssen, E. L. Scott, J. P. M. Sanders, *ChemSusChem* **2011**, *4*, 785-791.
[17]   J. Le Nôtre, E. L. Scott, M. C. R. Franssen, J. P. M. Sanders, *Green Chem.* **2011**, *13*, 807-809.
[18]   Y. Teng, E. L. Scott, J. P. M. Sanders, *J. Chem. Technol. Biotechnol.* **2012**, *87*, 1458-1465.
[19]   J. Deng, Q.-G. Zhang, T. Pan, Q. Xu, Q.-X. Guo, Y. Fu, *RSC Adv.* **2014**, *4*, 27541-27544.
[20]   J. E. Holladay, T. A. Werpy, D. S. Muzatko, *Appl. Biochem. Biotechnol.* **2004**, *115*, 857-869.
[21]   F. D. Schouwer, L. Claes, N. Claes, S. Bals, J. Degrève, D. E. De Vos, *Green Chem.* **2015**, *17*, 2263-2270.
[22]   N. Yamano, N. Kawasaki, S. Takeda, A. Nakayama, *J Polym. Environ.* **2013**, *21*, 528–533.
[23]   S. J. Park, E. Y. Kim, W. Noh, Y. H. Oh, H. Y. Kim, B. K. Song, K. M. Cho, S. H. Hong, S. H. Lee, J. Jegal, *Bioprocess Biosyst. Eng.* **2013**, *36*, 885–892.
[24]   K. Hashimoto, T. Hamano, M. Okada, *J. Appl. Polymer. Sci.* **1994**, *54*, 1579-1583.
[25]   T. M. Lammens, M. C. R. Franssen, E. L. Scott, J. P. M. Sanders, *Green Chem.* **2010**, *12*, 1430-1436.
[26]   D. J. Morgan, *Surf. Interface Anal.* **2015**, *47*, 1072-1079.
[27]   G. Schön, *J. Electron. Spectrosc.* **1972**/**1973**, *1*, 377-387.
[28]   J. M. Tura, P. Regull, L. Victori, M. D. De Castellar. *Surf. Interface Anal.*, **1988**, *11*, 447-449.
[29]   J. L. G. Fierro, J. M. Palacios, F. Tomas, *Surf. Interface Anal.* **1988**, *13*, 25-32.
[30]   M. Meng, L. Stievano, J.-F. Lambert, *Langmuir* **2004**, *20*, 914-923.
[31]   K. Fujimoto, M. Kameyama, T. Kunugi, *J. Catal.* **1980**, *61*, 7-14.
[32]   S. Scirè, C. Crisafulli, R. Maggiore, S. Minicò, S. Galvagno, *Catal. Lett.* **1998**, *51*, 41-45.
[33]   M. Kim, W-.S. Sim, D. A. King, *J. Chem. Soc. Faraday Trans.* **1996**, *92*, 4781-4785.
[34]   H. Yoshida, S. Narisawa, S. Fujita, L. Ruixia, M. Arai, *Phys. Chem. Chem. Phys.* **2012**, *14*, 4724-4733.
[35]   M. A. Henderson, S. D. Worley, *Surface Sci.* **1985**, *149*, L1-L6.
[36]   D. W. McKee, *J. Catal.* **1967**, *8*, 240-249.
[37]   M. A. Vannice, *J. Catal.* **1975**, *37*, 462-473.
[38]   M. A. Vannice, *J. Catal.* **1975**, *37*, 449-461.
[39]   R. M. Lukes, C. L. Wilson, *J. Am. Chem. Soc.* **1951**, *73*, 4790-4794.
[40]   W. H. Bagnall, E. P. Goodings, C. L. Wilson, *J. Am. Chem. Soc.* **1951**, *73*, 4794-4798.
[41]   J. Verduyckt, R. Coeck, D. E. De Vos, *ACS Sustainable Chem. Eng.* **2017**, *5*, 3290-3295.
[42]   T. Mizugaki, K. Togo, Z. Maeno, T. Mitsudome, K. Jitsukawa, K. Kaneda, *Sci. Rep.* **2017**, *7*, 1-6.
[43]   G. C. Bond, In *Catalysis by Metals*, Academic Press: London and New York, **1962**, p 65-68.
[44]   A. Guerreo-Ruiz, *React. Kinet. Catal. Lett.* **1993**, *49*, 53-60.
[45]   C. S. Kellner, A. T. Bell, *J. Catal.* **1981**, *70*, 418-432.
[46]   A. Hess, E. Kemnitz, A. Lippitz, W. E. S. Unger, D.-H. Mentz, *J. Catal.* **1994**, *148*, 270-280.

Entry for the Table of Contents

FULL PAPER

Glutamic acid, an abundant non-essential amino acid, was converted into 2-pyrrolidone through successive reactions over Ru/Al$_2$O$_3$ under pressurized hydrogen atmosphere. The conversion of pyroglutaminol into 2-pyrrolidone was a key reaction in the reaction pathway, and Ru/Al$_2$O$_3$ exhibited high activity due to remarkable effect of CO activation.
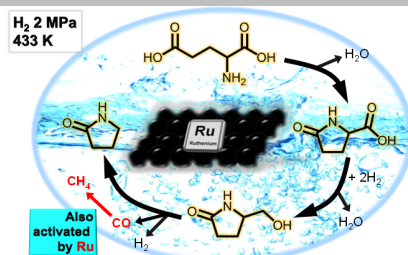
S. Suganuma*, A. Otani, S. Joka, H. Asako, R. Takagi, E. Tsuji, N. Katada

Page No. – Page No.

Title

One-step conversion of glutamic acid into 2-pyrrolidone on supported Ru catalyst in hydrogen atmosphere: remarkable effect of CO activation