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Journal Name

COMMUNICATION

Conversion of 5-Hydroxymethylfurfural to a Cyclopentanone Derivative by Ring Rearrangement over Supported Au Nanoparticles

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Journal Name

COMMUNICATION

Supported Au nanoparticles showed efficient catalytic performance for the ring rearrangement of 5-hydroxymethylfurfural (HMF) to a cyclopentanone derivative, 3-hydroxymethylcyclopetanone (HCPN), by taking advantage of the selective hydrogenation on Au nanoparticles and the Lewis acid catalysis of metal oxide supports. Among various metal oxides supported Au catalysts, the highest yield of HCPN was obtained by using Au/Nb$_2$O$_5$ (86% yield).

Biorefinery is being intensely investigated as a key technology for sustainable future. In the biorefinery process, 5-hydroxymethylfurfral (HMF), which can be synthesized by dehydration of hexoses, is regarded as one of the most promising precursor to produce valuable chemicals and fuels.[1-3] For example, by oxidation reaction, HMF is converted to 2,5-furandicarboxylic acid which is a potential alternative to terephthalic acid.[4] Hydrogenation and/or hydrogenolysis of HMF give 2,5-bis(hydroxymethyl)furan (BHF), 2,5-bis(hydroxymethyl)tetrahydrofuran (BHTF), 1,6-hexandiol, and 2,5-dimethylfuran (DMF), etc., which can be used for polymers, fine chemicals, and fuels.[5-9] Aldol condensation of HMF with acetone on acid-base catalyst and the following hydrogenation and hydrogenolysis provide jet fuel.[10] In the similar fashion, furfural synthesized by dehydration of pentose can be also converted to valuable compounds. Very recently, the ring rearrangement of furfural has attracted increasing attention as a new transformation of biomass derived material to useful chemicals.[11-14] Hronec et al. reported the rearrangement of furan ring of furfural to cyclopentanone over supported platinum group metal catalysts (Pt, Pd, and Ru), and carbon supported Pt (Pt/C) provided the highest yield of cyclopentanone.[15, 16] The rearrangement of furan ring is considered to proceed via selective hydrogenation of aldehyde to
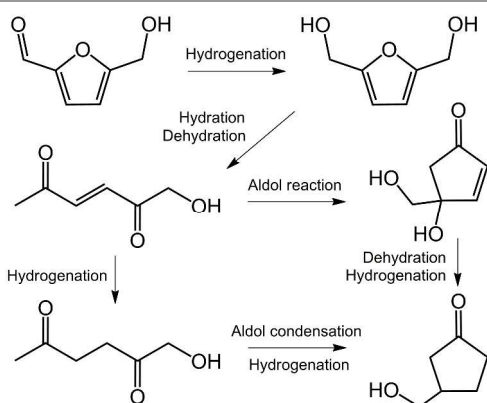
Scheme 1 Hydrogenation and ring rearrangement of HMF to HCPN.

alcohol and the following ring opening and closing reactions (Scheme 1). It is well known that platinum group metal catalysts show high

hydrogenation activity but low selectivity towards hydrogenation of a multi-functional compound.[17, 18] The low selectivity would decrease the preferential synthesis of cyclopentanone from furfural due to the hydrogenation of furan ring. Yang et al. reported that Ni-Cu bimetallic catalyst, which is known for the selective hydrogenation of furfural to furfuryl alcohol in gas-phase, exhibited the ring rearrangement reaction of furfural to give high yield of cyclopentanone (62%) in aqueous solution; however, the Ni-Cu catalyst did not convert HMF to a cyclopentanone derivative at al.[12] Au catalyst is also known for the selective hydrogenation of unsaturated aldehyde.[18-21] In addition to the selective hydrogenation, acid-base property of supports can promote the ring opening and closing reaction.[5, 6] Thus, Au supported on metal oxides with acid-base property is expected to show efficient performance for the ring rearrangement reaction. However, to our knowledge, there is no report on the ring rearrangement reaction over supported Au catalysts as well as the support effect on the ring rearrangement reaction.

Previously, we demonstrated that Au/Al$_2$O$_3$ showed high catalytic activity and selectivity for the hydrogenation of HMF to BHF (> 96% yield).[5] The basic supports did not facilitate the ring opening reaction to provide BHF in high selectivity. On the other hand, the acidic supports promoted the ring-opening reaction to produce 1-hydroxyl-2,5-hexanedione (HHD), which has a potential to form ring compounds through intramolecular aldol condensation. Herein, we investigated the ring rearrangement of HMF over supported Au catalysts by taking advantage of the selective hydrogenation over Au and the acid-base property of supports. The present study first demonstrates the efficient ring rearrangement of HMF to a cyclopentanone drivertive, 3-hydroxymethylcyclopetanone (HCPN), which can be an intermediate chemical for fragrance, pesticide, and polymer.

Supported Au catalysts were prepared by deposition precipitation method using HAuCl$_4$ as a precursor containing 10 mg of Au and 0.99 g of various metal oxide supports (Nb$_2$O$_5$, Al$_2$O$_3$, ZrO$_2$, TiO$_2$, SiO$_2$-Al$_2$O$_3$ (SA), La$_2$O$_3$, CeO$_2$, hydrotalcite (HT)).[22] The catalysts were calcined at 573 K under air for 3 h, and treated by H$_2$ for 1 h and then O$_2$ for 0.5 h at 473 K prior to the reaction. This pretreatment is different from that for the preparation of Au subnanoparticles which provided high BHF yield in the previous study. The pretreatment will increase rather than decrease the particle size; however, such small Au particles were not required for the ring rearrangement reaction as described below. The catalytic reaction was performed under the following conditions: 10 mg of supported gold catalysts; 3 mL of 0.067 M HMF aqueous solution; 8 MPa of H$_2$; 413 K. In this study, we identified 4-hydroxy-4-hydroxymethyl-2-cyclopentenone (HCPEN) as an intermediate for production of HCPN.

Table 1 lists the results of the ring rearrangement reaction over the various metal oxides supported Au catalysts (entries 1-8). The highest yield of HCPN was obtained on Au/Nb$_2$O$_5$ among the Au catalysts

(86%). Au/Nb_2O_5 was reusable without any decrease in the initial conversion of HMF and the yield of HCPN (Table 1 entries 9-11). No decrease in the initial conversion of HMF (Table 1 entries 10, 11) suggests that the gold nanoparticles of Au/Nb_2O_5 do not grow during the reaction, and their hydrogenation activity does not decrease. Actually, particle size analysis by TEM showed that the size of gold nanoparticle did not change by the reaction for 12 h (Figure S1). The ICP analysis (Table S1) indicated that the Au loading of Au/Nb_2O_5 did not change after the reaction (0.56wt% of Au loading). The result indicates no leaching of gold during the reaction.

The Au supported on Al_2O_3, ZrO_2, TiO_2, and SA also gave HCPN with relatively high yield. These metal oxide supports including Nb_2O_5 are conventionally known to have acid property. On the other hand, the Au supported on basic supports, CeO_2, La_2O_3, and HT, provided ring rearranged products (HCPN and HCPEN) at much lower yield in comparison with the acid metal oxide supported Au catalysts. The results suggest that the acid on metal oxide supports promotes the ring-opening and closing reaction (hydration and dehydration). It should be also mentioned that, in our previous study, Au/Al_2O_3 provided BHF, but, in the present study, gave HCPN with high yield. This is because the longer reaction time in this study caused the ring opening and closing on Al_2O_3 which has not only base sites but also acid sites.

The time course of the conversion of HMF to the product yields on Au/Nb_2O_5 is shown in Fig. 1. As HMF was consumed, the yields of BHF and HCPEN increased for ca. 1 h, and HHD for ca. 6 h. The yields of these intermediates decreased and the yield of HCPN increased up to 86% for 12 h. On the basis of the result, we proposed that HCPN is produced by a stepwise reaction as shown in Scheme 1. The selective hydrogenation over Au gives BHF. The furan ring of BHF opens on acid sites of the supports to provide 1-hydroxy-3-hexene-2,5-dione (HHED) (not detected); Hydrogenation of HHED produces HHD, and intramolecular aldol condensation of HHD over supports and the following hydrogenation generate HCPN. On the other hand, intramolecular aldol reaction of HHED also proceeds to give HCPEN. The resulting HCPEN is dehydrated and hydrogenated to produce HCPN.[12, 23] In this scheme, the acidity of the supports first works for the ring opening reaction, and then the aldol reaction and dehydration. As shown above, the basic metal oxides supported Au catalysts gave low yield of the ring rearrangement products (HCPEN and HCPN). This would be due to low catalytic activity of basic metal oxides for the ring opening of BHF. In fact, it has been reported that the ring opening of BHF proceeds on acidic supports, but does not on basic supports.[5, 6] Therefore, the acid property of support is necessary for the ring rearrangement and generation of HCPN. The reaction for more than 12 h decreased HCPN yield (45% of HCPN yield for 72 h). Although the products were not currently identified, 3-hydroxymethylcyclopentanol might be formed by hydrogenation of HCPN.

The reaction without the supported Au catalysts showed no yield of HCPN (Table 1 entry 12). In addition, the reaction with only Nb_2O_5 or without H_2 (under N_2) gave no HCPN (Table 1 entries 13 and 14). The results indicate that the hydrogenation of HMF on Au is required to generate HCPN. In these control experiments, the color of reaction solutions changed from yellow to dark yellow, and some conversion of HMF was observed. It is possible that HMF was polymerized by heat

and the catalysts. The reaction was also carried out using Nb_2O_5 supported Pt, Pd, and Ru which are known to have high catalytic activity for hydrogenation reaction. The Nb_2O_5 supported Pt, Pd, and Ru catalysts were prepared by the conventional impregnation method or deposition precipitation method. Prior to the reaction, the catalysts were treated with H_2 for 1 h and then O_2 for 0.5 h at 473 K. The Pt, Pd, and Ru catalysts provided 28, 43, and 66% yield of HCPN, respectively (Table 1 entries 15-17). Compared with them, higher HCPN yield was obtained on Au/Nb_2O_5. The selective hydrogenation of HMF over Au is considered to promote the efficient transformation of HMF to HCPN. Interestingly, although the O_2 treatment for Au/Nb_2O_5 prior to the reaction almost did not affect the HCPN yield (Table 1 entries 1 and 18), the pretreatment for Pt/Nb_2O_5 improves the HCPN yield (Table 1 entries 15 and 19). It is likely that (partially) oxidized Pt enhances the selective hydrogenation. The variation of catalysis with the pretreatment condition is a subject for future study.

Table 1. Results for conversion of HMF into HCPN in the presence of various metal oxides supported Au catalysts and Nb_2O_5 supported Pt, Pd, and Ru. [a]

Entry	Catalyst	Conversion (%)	Yield (%) [b]			
			HCPN	HHD	BHF	HCPEN
1	Au/Nb_2O_5	>99	86	7	0	0
2	Au/Al_2O_3	>99	72	3	0	0
3	Au/ZrO_2	>99	62	1	0	0
4	Au/TiO_2	>99	54	4	0	0
5	Au/SA	92	1	16	1	0
6	Au/La_2O_3	89	1	3	0	13
7	Au/CeO_2	92	1	2	0	9
8	Au/HT	98	0	1	16	13
9 [c]	Recycled Au/Nb_2O_5	>99	84	10	0	0
10 [d]	Au/Nb_2O_5	37	1	3	5	8
11 [e]	Recycled Au/Nb_2O_5	40	2	5	3	9
12	Blank	10	0	0	0	0
13	Nb_2O_5	11	0	0	0	0
14 [f]	Au/Nb_2O_5	24	0	0	0	0
15	Pt/Nb_2O_5	>99	28	0	0	0
16	Pd/Nb_2O_5	>99	43	7	0	0
17	Ru/Nb_2O_5	>99	66	2	0	0
18 [g]	Au/Nb_2O_5 without O_2 treatment	>99	82	5	0	0
19 [g]	Pt/Nb_2O_5 without O_2 treatment	>99	4	27	0	0
20 [h]	Au/Nb_2O_5 + 8.5 mM H_3PO_4	81	1	60	0	6

[a] Reaction conditions: Catalyst 10 mg, 0.067 M HMF aqueous solution 3 mL, H_2 8 MPa, 413 K, 12 h. [b] Yield: (mol product)/(mol initial HMF)×100, HMF: 5-hydroxymethylfurfural, HCPN: 3-hydroxymethylcyclopetanone, HHD: 1-hydroxyl-2,5-hexanedione, BHF: 2,5-bishydroxymethylfuran, HCPEN: 4-hydroxy-4-hydroxymethyl-2-cyclopentenone. [c] Au/Nb_2O_5 was recycled by washing with acetone and water, and dryness at 353 K. [d] Reaction time: 1h. [e] Recycle test. Reaction time: 1h. [f] The catalytic test was performed under N_2 without H_2. [g] The catalysts were pretreated with H_2 but without O_2. [h] The catalytic test was carried out in the presence of 8.5 mM of H_3PO_4.
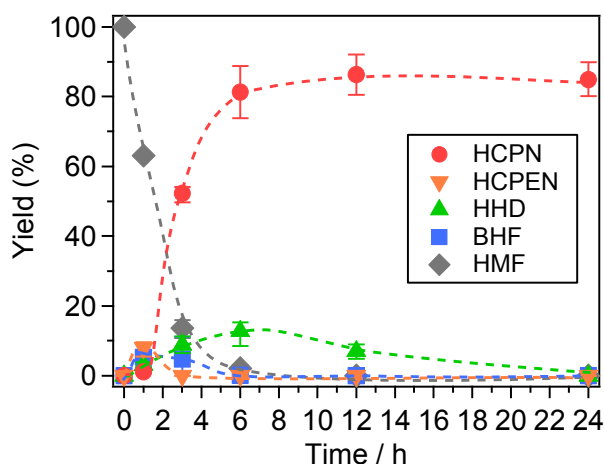
Fig. 1 Time course of the yields of HCPN (●), HCPEN (▼), HHD (■), BHF (▲), HMF (◆) for the ring rearrangement reaction over Au/Nb$_2$O$_5$. The catalyst test at each time was carried out at least three times, and the error bars represent the minimum to maximum values.
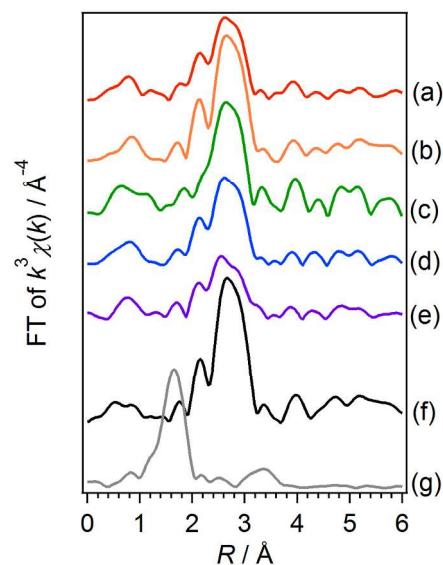
Our previous study demonstrated that the catalytic activity for the selective hydrogenation of HMF to BHF over Au/Al$_2$O$_3$ significantly depends on the Au particle size.[5] Thus, we investigated the Au particle size effect on the HCPN yield. The Au particle size was evaluated from the extended X-ray absorption fine structure (EXAFS) spectral analysis (Fig. S1). Fig. 2 shows the Fourier transformed Au L$_3$-edge EXAFS spectra of Au/Nb$_2$O$_5$, Au/Al$_2$O$_3$, Au/ZrO$_2$, Au/TiO$_2$, and Au/SA, which gave HCPN (Table 1), together with Au foil and Au$_2$O$_3$ as references. All of the samples showed the peak around 2.6 Å derived from Au-Au scattering of Au metal. The peak intensities of the samples were smaller than that of Au foil, indicating that the samples are composed of Au nanoparticles supported on metal oxides. The peak intensity of the Au-Au scattering and the coordination number (Au-Au pair) determined by curve fitting analysis (Table S2) increased in the order of Au/SA < Au/Nb$_2$O$_5$ < Au/TiO$_2$ < Au/ZrO$_2$ < Au/Al$_2$O$_3$, which represents the order of the size of Au nanoparticles. The size of Au nanoparticles of Au/SA and Au/Nb$_2$O$_5$ were estimated to be ca. 2-3 nm, and those for the other catalysts to be larger than 3 nm, assuming that the Au nanoparticles have cuboctahedral structure.[24] Noted that the Au particle size had no relation to HCPN yield (Table 1), although our previous study showed that small Au nanoparticles have high catalytic performance for the selective hydrogenation of HMF to BHF. It is reasonable to conclude that the selective hydrogenation on Au nanoparticles triggers the formation of HCPN, but the hydrogenation rate varied with Au particle size does not significantly affect the yield of HCPN.

Based on the above results, we concluded that the acid property of catalysts mainly controls HCPN yield. For further investigation of the effect of acidity on the HCPN formation, we carried out the ring rearrangement reaction on Au/Nb$_2$O$_5$ in the presence of a liquid Brønsted acid, H$_3$PO$_4$. As a result, the addition of H$_3$PO$_4$ reduced the yield of HCPN (Table 1 entry 20). It is suggested that Brønsted acidity does not contribute the HCPN formation. Fig. 3 shows the Fourier transformed infrared (FT-IR) spectra of pyridine adsorbed on the supported Au catalysts which provided HCPN. Although Au/SA showed the small band assignable to the ring stretching ν19b of

pyridine adsorbed on Brønsted acid site at 1545 cm^{-1}, the other supported Au catalysts presented almost no band at around 1545 cm^{-1}. On the other hand, the strong band at 1440-1455 cm^{-1} assignable to the ν19b mode of pyridine adsorbed on Lewis acid site was observed on all of the catalysts. It is noteworthy that Au/Nb$_2$O$_5$, which gave the highest HCPN yield, presented strong band of pyridine on Lewis acid site, but almost no band of pyridine on Brønsted acid. These results indicate that the ring rearrangement reaction proceeds on Lewis acid sites. Recently, Nb$_2$O$_5$ has been reported to have unique Lewis acid sites working in water.[25, 26] Such Lewis acid sites might contribute to the high yield of HCPN.

In summary, we first demonstrated the ring rearrangement of HMF to HCPN over supported Au catalysts by taking advantage of the selective hydrogenation on Au and the Lewis acid catalysis of metal oxide supports. Among the Au catalysts, Au/Nb$_2$O$_5$ exhibited the highest catalytic performance for the ring rearrangement, and gave 86% yield of HCPN. The ring rearrangement of HMF over Au catalysts proposed in this study can contribute development of the biorefinery for sustainable future.

Fig. 2 FT of Au L$_3$-edge EXAFS spectra of Au supported on (a) Nb$_2$O$_5$, (b) Al$_2$O$_3$, (c) ZrO$_2$, (d) TiO$_2$ and (e) SA, together with (f) Au foil and (g) Au$_2$O$_3$ as references.
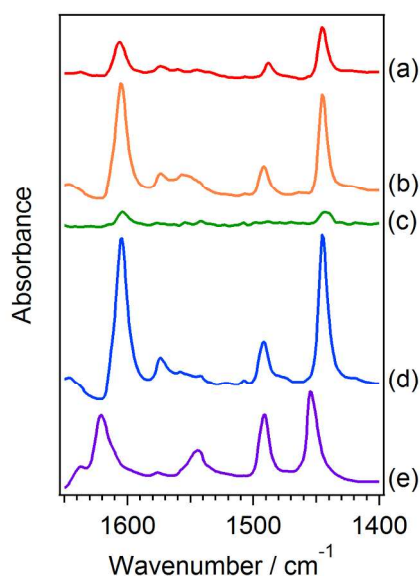
Fig. 3 FT-IR spectra of pyridine adsorbed on (a) Nb_2O_5, (b) Al_2O_3, (c) ZrO_2, (d) TiO_2, and (e) SA supported Au catalysts.

Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental procedures; ICP analysis of Au catalysts; NMR of HCPN, HCPEN, HHD, and BHF; TEM images of Au/Nb_2O_5 before and after the reaction; Au L_3 edge EXAFS and XANES spectra of Au catalysts; Result of curve fitting analysis of the EXAFS spectra. See DOI: 10.1039/c000000x/

1. A. Corma, S. Iborra and A. Velty, *Chem. Rev.*, 2007, **107**, 2411.
2. J. N. Chheda, G. W. Huber and J. A. Dumesic, *Angew. Chem. Int. Ed.*, 2007, **46**, 7164.
3. R.-J. van Putten, J. C. van der Waal, E. de Jong, C. B. Rasrendra, H. J. Heeres and J. G. de Vries, *Chem. Rev.*, 2013, **113**, 1499.
4. N. K. Gupta, S. Nishimura, A. Takagaki and K. Ebitani, *Green Chemistry*, 2011, **13**, 824.
5. J. Ohyama, A. Esaki, Y. Yamamoto, S. Arai and A. Satsuma, *RSC Advances*, 2013, **3**, 1033.
6. R. Alamillo, M. Tucker, M. Chia, Y. Pagan-Torres and J. Dumesic, *Green Chemistry*, 2012, **14**, 1413.
7. Y. Nakagawa and K. Tomishige, *Catal. Commun.*, 2010, **12**, 154.
8. M. Chia, Y. J. Pagan-Torres, D. Hibbitts, Q. Tan, H. N. Pham, A. K. Datye, M. Neurock, R. J. Davis and J. A. Dumesic, *J. Am. Chem. Soc.*, 2011, **133**, 12675.
9. Y. Roman-Leshkov, C. J. Barrett, Z. Y. Liu and J. A. Dumesic, *Nature*, 2007, **447**, 982.
10. J. N. Chheda and J. A. Dumesic, *Catal. Today*, 2007, **123**, 59.
11. L. Bui, H. Luo, W. R. Gunther and Y. Román-Leshkov, *Angew. Chem. Int. Ed.*, 2013, **52**, 8022.
12. Y. Yang, Z. Du, Y. Huang, F. Lu, F. Wang, J. Gao and J. Xu, *Green Chemistry*, 2013, **15**, 1932.
13. S. Sato, J. Igarashi and Y. Yamada, *Appl. Catal., A*, 2013, **453**, 213.
14. T. Buntara, S. Noel, P. H. Phua, I. Melián-Cabrera, J. G. de Vries and H. J. Heeres, *Angew. Chem. Int. Ed.*, 2011, **50**, 7083.
15. M. Hronec and K. Fulajtarova, *Catal. Commun.*, 2012, **24**, 100.
16. M. Hronec, K. Fulajtarova and T. Liptaj, *Appl. Catal., A*, 2012, **437-438**, 104.
17. A. Corma and P. Serna, *Science*, 2006, **313**, 332.
18. E. Bus, R. Prins and J. A. van Bokhoven, *Catal. Commun.*, 2007, **8**, 1397.
19. J. E. Bailie and G. J. Hutchings, *Chem. Commun.*, 1999, 2151.
20. J. E. Bailie, H. A. Abdullah, J. A. Anderson, C. H. Rochester, N. V. Richardson, N. Hodge, J.-G. Zhang, A. Burrows, C. J. Kiely and G. J. Hutchings, *PCCP*, 2001, **3**, 4113.
21. C. Milone, M. L. Tropeano, G. Gulino, G. Neri, R. Ingoglia and S. Galvagno, *Chem. Commun.*, 2002, 868.
22. M. Haruta, *Catal. Today*, 1997, **36**, 153.
23. Y. Nakagawa, M. Tamura, K. Tomishige, *ACS Catalysis* 2013, **3**, 2655.
24. J. Ohyama, K. Teramura, S-i. Okuoka, S. Yamazoe, K. Kato, T. Shishido, T. Tanaka, *Langmuir*, 2010, **26**, 13907.
25. K. Nakajima, Y. Baba, R. Noma, M. Kitano, J. N. Kondo, S. Hayashi and M. Hara, *J. Am. Chem. Soc.*, 2011, **133**, 4224.
26. Y. Koito, K. Nakajima, M. Kitano and M. Hara, *Chem. Lett.*, 2013, **42**, 873.