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Effect of Heterogeneous Acid-Base Catalysis on Conversion of 5-Hydroxymethylfurfural into A Cyclopentanone Derivative

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Effect of heterogeneous acid-base catalysis on conversion of 5-hydroxymethylfurfural (HMF) to 3-hydroxymethylcyclopetanone (HCPN) was investigated. It was demonstrated that the acidic metal oxides, in particular, Ta_2O_5, significantly enhanced the yield of HCPN due to its moderate Lewis acidity.

Biorefinery is getting more and more attention for production of sustainable chemicals and fuels.[1, 2] Cellulose and hemicellulose from woody biomass can be converted to furan derivatives, 5-hydroxymethylfurfral (HMF) and furfural (FA), through catalytic reactions including hydrolysis, isomerization, and dehydration.[3, 4, 5, 6] The furan derivatives are regarded as platform chemicals in the biorefinery process: for example, hydrogenation and/or hydrogenolysis of HMF produce 2,5-bis(hydroxymethyl)furan (BHF), 2,5-bis(hydroxymethyl)tetrahydrofuran (BHTF), 1,6-hexandiol, and 2,5-dimethylfuran (DMF), which can be utilized for polymers, fine chemicals, and fuels.[5, 7, 8, 9, 10, 11]

Very recently, the ring rearrangement of the furan derivatives has been developed as a new reaction in the biorefinery.[2, 12, 13, 14, 15, 16, 17, 18, 19, 20] By the ring rearrangement reaction, HMF and FA can be transformed to cyclopentanone or its derivatives, which can be an intermediate chemical for fragrance, pesticide, polymer, and solvent. In the current petrochemical process, cyclopentanone and its derivatives have been produced from adipic acid, which can be produced from cyclohexanol or cyclohexane.[21] In the economic point of view, the synthesis of cyclopentanone derivatives from HMF and FA is interesting, since the biomass derived chemicals (HMF, FA) have potential to be cheaper than the petrochemical (adipic acid) with depletion of oil resources and with the development of biorefinery process. In addition, as an intermediate chemical compound (e.g., for fragrance), HCPN may be a value-added cyclopentanone, because HCPN is a β-substituted cyclopentanone which is difficult to synthesize from cyclopentanone although a α-substituted cyclopentanone is relatively easily synthesized.[21]

Several research groups have reported catalytic conversion of FA to cyclopentanone (CPO) or cyclopentanol (CPL) using heterogeneous catalysts such as a carbon supported Pt,[12, 15] SBA-15 supported Ni-Cu catalysts,[16] Cu-Co catalysts,[18] and CuZnAl catalysts.[17] Meanwhile, we have reported the conversion of HMF to 3-hydroxymethylcyclopetanone (HCPN) using supported Au catalysts.[20] The rearrangement of furfural derivatives is considered to proceed through hydrogenation of the aldehyde group and the following ring opening and closing reactions accompanied with hydration and dehydration (Scheme 1, which is improved from our previously reported one: In the present study, 3-hydroxymethyl-(2, 3, or 4)-cyclopentenone (HCPEN) was newly suggested as an intermediate based on mass spectroscopy). The scheme suggests that the catalyst system for the ring rearrangement should have not only hydrogenation activity but also acid-base catalysis. In the case of the ring rearrangement of FA, it has been proposed that H_2O in a reaction system acts as acid-base catalyst, and additional acid-base catalysts are not necessary to obtain CPO.[15, 16] On the other hand, our previous study on the ring rearrangement of HMF using various metal oxides supported Au catalysts implied that acid-base catalysis of the metal-oxide-supports contributes to efficient production of HCPN.[20] However, in the previous study, we could not clearly discuss the effect of acid-base catalysis on the metal oxides on the ring rearrangement of HMF, since the various supported Au catalysts did not have an identical hydrogenation activity due to different sizes and/or chemical states of Au nanoparticles between the various supported Au catalysts.

In the present study, in order to investigate the effect of acid-base catalysis on the ring rearrangement of HMF, we performed the reaction using a combination catalyst system that is composed of a metal oxide as an acid-base catalyst; Pt supported on an inert metal oxide (Pt/SiO_2) as a hydrogenation

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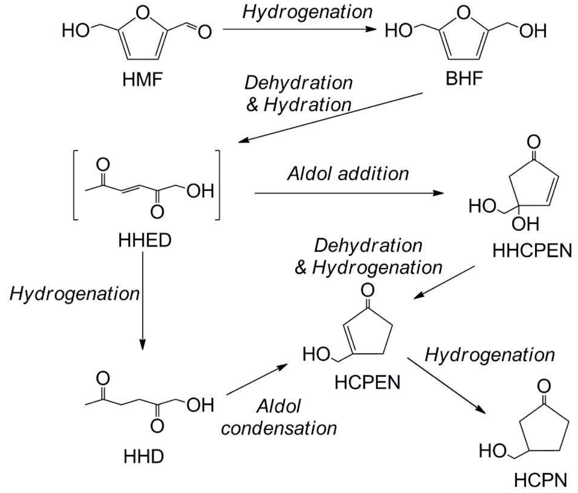
Electronic Supplementary Information (ESI) available: experimental details; pH of the reaction solutions; duplicate test; plot of HHF yield against pyridine IR peak; recycle test. See DOI: 10.1039/x0xx00000x catalyst. As the acid-base metal oxides, Ta_2O_5, ZrO_2, Nb_2O_5, TiO_2, Al_2O_3, and SiO_2-Al_2O_3, CeO_2, La_2O_3, and hydrotalcite were applied to the reaction. As a result, the acidic metal oxides, in particular, Ta_2O_5, enhanced the ring rearrangement of HMF to HCPN. We also investigated the effective acidity for the reaction by means of Fourier transformed infrared (FT-IR) spectroscopy using pyridine as a probe molecule.



Scheme 1. Conversion of HMF to HCPN.

All of the above metal oxides were calcined at 500˚C before use. Pt/SiO_2 (1 wt% of Pt loading) was prepared by an impregnation method using $Pt(NH_3)_4Cl_2 \cdot 4H_2O$ as a precursor. Prior to catalytic tests, Pt/SiO_2 was pretreated under H_2 at 200˚C. Subsequently, Pt/SiO_2 was treated under O_2 at 200˚C, since our previous study suggested that the O_2 treatment of supported Pt catalysts is effective for selective hydrogenation of HMF to BHF.[20] The treated Pt/SiO_2 (10 mg), a metal oxide (10 mg), and an aqueous solution of HMF (0.067 M, 3 mL) were added to an autoclave (30mL, Taiatsu Techno Co., TVS-1 type). The reactor was pressurized with 3 MPa of H_2, and the reaction was carried out at 140˚C.

Fig. 1 exhibits the product distributions obtained by the reaction using Pt/SiO_2 with/without the various metal oxides. The reaction over any catalysts converted all of HMF, and provided 3-hydroxymethylcyclopentanone (HCPN), 3-hydroxymethyl-(2, 3, or 4)-cyclopentenone (HCPEN), 4-hydroxy-4-hydroxymethyl-2-cyclopentenone (HHCPEN), hydroxyl-2,5-hexanedione (HHD), 2,5-bis(hydroxymethyl)furan (BHF), 1,2,6-hexyanetrial, and undetectable or unidentified bi-products (possibly humins generated by cross-polymerization of the reactant and the intermediates.[22] The reaction using only Pt/SiO_2 (without metal oxides) produced a low yield of HCPN (7%). The presence of CeO_2, La_2O_3, and hydrotalcite, which are basic metal oxides, did not lead a large increase of the yield of HCPN (less than 25%). On the other hand, the presence of Ta_2O_5, ZrO_2, Nb_2O_5, TiO_2, Al_2O_3, and SiO_2-Al_2O_3, which are known to have acidic character more prominently than CeO_2, La_2O_3, and hydrotalcite,[23, 24, 25, 26] largely increased the HCPN yield. In particular, Ta_2O_5, ZrO_2, and Nb_2O_5 significantly enhanced the HCPN yield (72-82%). It has been reported that acid facilitates the ring-opening of BHF.[27] This is one of the reasons for the relatively high yield of HCPN on the acidic metal oxides.

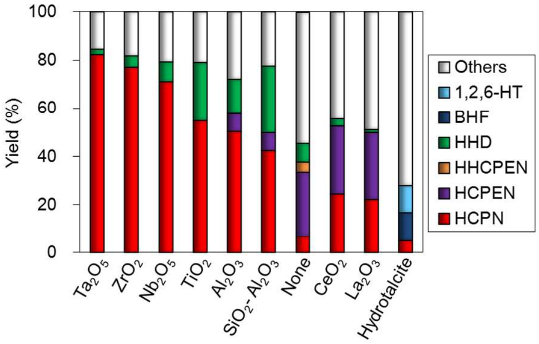


Fig. 1. Product distributions obtained by the reaction using Pt/SiO_2 with/without various metal oxides. Reaction condition: HMF aq. (0.067 M, 3 mL); Pt/SiO_2 (10 mg); a metal oxide (10 mg); H_2 3 MPa; 140˚C; 12 h. Since HMF was completely converted for 12 h over all catalysts, the yields mean the selectivity.

The pH of the reaction solution with various catalysts was measured (Fig. S1). The pH of the solution in the presence of Ta_2O_5, Nb_2O_5, TiO_2, ZrO_2, Al_2O_3, SiO_2-Al_2O_3, and CeO_2 with Pt/SiO_2 (pH = ca. 4 - 5) did not significantly change from the pH in the presence of only Pt/SiO_2 (pH = ca. 4). When La_2O_3 and hydrotalcite were added, the pH (ca. 7-11) increased from that of the reaction solution with Pt/SiO_2. Although the pH did not significantly change by addition of Ta_2O_5, Nb_2O_5, TiO_2, ZrO_2, Al_2O_3, and SiO_2-Al_2O_3, the yield of HCPN largely increased. It should be also noted that the addition of La_2O_3 increased the yield of HCPN (as well as the total yield of the ring rearranged products (HCPN+HCPEN)) in spite of the increase of the pH. It is suggested that another factor than the pH (ca. 4 - 8), that is, the Lewis acid on metal oxide surface, is important for production of HCPN as discussed later. On the other hand, the pH in the presence of hydrotalcite was much larger (pH = ca. 11) than that in the presence of Pt/SiO_2, and the yield of HCPN (and the total yield of the ring rearranged products) was smaller than that in the presence of Pt/SiO_2. In addition, the reaction using hydrotalcite gave 1,2,6-hexanetriol, which can be produced through total hydrogenation of BHF and following hydrogenolysis.[28] Therefore, the strong basicity of the reaction solution or the catalyst surface lead the different reaction of BHF.

For comparison to the results in Fig. 1, the reaction was performed using Au/Nb_2O_5 which showed high performance for HCPN production in our previous work. The HCPN yield on Au/Nb_2O_5 was 61%, and smaller than that reported previously (86%),[20] probably owing to the milder condition of the present work (3 MPa of H_2, 140˚C) than the previous one (8 MPa of H_2, 160˚C). As a result, the HCPN yields obtained on some of the present catalysts (Pt/SiO_2 + Ta_2O_5, ZrO_2, or Nb_2O_5) were higher than that on Au/Nb_2O_5 (61%). Usually, Pt catalysts have higher catalytic activity for hydrogenation than Au catalysts. The high catalytic activity of Pt catalysts would contribute to the high yield of HCPN in the milder reaction condition of this work.

Fig. 2(a) shows the time course of the reactant and product yields on the hydrogenation and ring rearrangement reaction using Pt/SiO_2 and Ta_2O_5. In the first 1 h, 77% of HMF was consumed to produce BHF (44% yield), HHCPEN (2%), HCPEN (10%), and HHD (2%). Then, BHF, HHCPEN, and HCPEN were consumed to form HCPN. The yield of HHD slightly increased at 3 h, and then plateaued. This time course is well consistent with that on Au/Nb_2O_5 reported previously.[20] Accordingly, the hydrogenation and ring-rearrangement reaction is considered to proceed as Scheme 1: The selective hydrogenation of HMF produces BHF; The furan ring of BHF opens to provide 1-hydroxy-3-hexene-2,5-dione (HHED) (not detected, represented in parentheses in Scheme1); Intramolecular aldol reaction of HHED gives HHCPEN; HHCPEN is dehydrated and hydrogenated to produce HCPEN; HCPEN is hydrogenated to form HCPN. HCPN is also considered to be produced through HHD formed by hydrogenation of HHED: intramolecular aldol condensation of HHD and the following hydrogenation produce HCPN. In the reaction scheme, Pt/SiO_2 facilitates the hydrogenation reaction, and Ta_2O_5 is considered to facilitate the steps involving acid-base catalysis, which are hydration, aldol reaction, and dehydration.

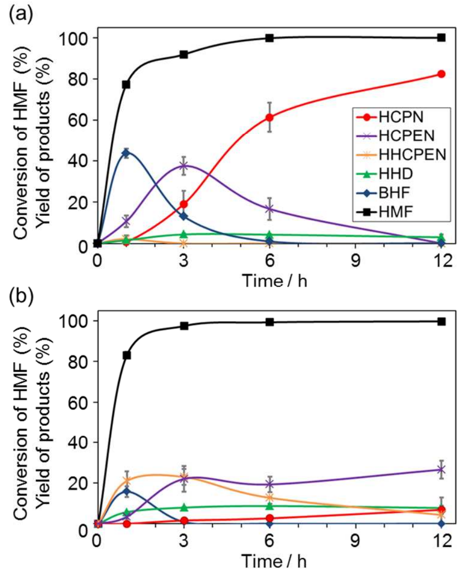


Fig. 2. Time courses of the conversion of HMF and the yields of the products on the ring rearrangement reaction using (a) Ta_2O_5 and Pt/SiO_2 and (b) only Pt/SiO_2. The conversions and yields are averages of two experiments (Figs. S2 and S3). The error bars indicate the difference between the two experiments.

The time course of HMF conversion and the product yields on Pt/SiO_2 was also examined for comparison. As shown in Fig. 2(b), HMF was converted to BHF, HHCPEN, HCPEN, and HHD in the first 1 h. It should be noted that the ring-opened and rearranged products were produced in the reaction without the acidic metal oxides. This result suggests that the ring opening and closing reactions proceeds in the absence of the acidic metal oxides. The yield of HHCPEN reached a peak at 3 h (21%) and then decreased, followed by increase of HCPEN and HCPN.

In comparison with Pt/SiO_2 without addition of metal oxides (Fig. 2(b)), Pt/SiO_2 with Ta_2O_5 showed lower yields of HHCPEN and HHD, and higher yield of HCPEN (Fig. 2(a)). It is suggested that Ta_2O_5 facilitates the reaction of HHED to HCPEN and the reaction of HHD to HCPEN, which involve aldol condensation and dehydration. As is the case with Ta_2O_5, the other acidic metal oxides will facilitate these intermediate steps to give relatively high yield of HCPN. Without the metal oxides, the intermediates (BHF, HHCPEN, and HHD) might be converted to humins,[22] although they could not be identified in this study.

Previously, several research groups have developed ring rearrangement reaction of furfural (FA) to cyclopentanone (CPO).[12, 13, 14, 15, 16, 17, 18] In the literature by Hronec et al., the conversion of FA to CPO proceeds on Pd supported on carbon, although carbon is usually less active or inert as an acid catalyst compared to the acidic metal oxides used in this study.[12, 15] Yang et al. demonstrated that the reaction of FA to CPO requires H_2, H_2O, and a catalyst for hydrogenation (Ni-Cu bimetallic catalyst supported on SBA-15 in their study); the addition of acid-base catalysts does not increase the yield of CPO.[16] It has been proposed that H_2O in the reaction system works as an acid catalyst in the conversion of FA to CPO.[15,16] Yang et al. also presented that the effective catalytic system for the conversion of FA to CPO does not work for the conversion of HMF to HCPN. On the other hand, we demonstrated that acid catalysts are necessary to obtain high yield of HCPN by facilitating the dehydration process. It is possible that the activation energies for aldol condensation and dehydration (HHED to HCPEN and HHD to HCPEN) are much larger than the corresponding activation energies for the ring rearrangement of FA. The acidic metal oxides will reduce the activation energies of those processes for HCPN production by their acid catalysis.

To investigate the effective acid for the production of HCPN, the acid type and strength of metal oxides was evaluated from the FT-IR spectra of pyridine adsorbed on the metal oxides shown in Fig. 3. All of the spectra showed bands at around 1445 cm^{-1} and 1610 cm^{-1} assignable to the ν_{19b} and ν_{8a} mode of pyridine adsorbed on Lewis acid site. The FT-IR spectrum of SiO_2-Al_2O_3 also exhibited a small band assignable to the ring stretching ν_{19b} mode of pyridine adsorbed on Brønsted acid site at around 1545 cm^{-1}, but the other metal oxides showed almost no band at around 1545 cm^{-1}. Since SiO_2-Al_2O_3 gave lower yield of HCPN than the other acidic metal oxides, the Lewis acid is considered to be responsible for the production of HCPN. It should be also noted that CeO_2, La_2O_3, and hydrotalcite showed the pyridine adsorbed on the Lewis acid sites. The presence of Lewis acid sites on the basic oxides can explain their production of HCPN, HCPEN, and HHD (Fig. 1).

The peak wavenumber of pyridine (ν_{8a}) adsorbed on Lewis acid sites at around 1610 cm^{-1} increased in the order of La_2O_3 < hydrotalcite < CeO_2 < TiO_2 < Nb_2O_5 ≈ ZrO_2 < Ta_2O_5 < Al_2O_3 < SiO_2-Al_2O_3. The higher wavenumber suggests stronger Lewis acid of metal oxides.[25, 29] To inspect the effect of Lewis acid strength on the production of HCPN, the HCPN yields (Fig. 1) were plotted against the peak wavenumbers of adsorbed pyridine (ν_{8a}) as shown in Fig. 4. The plot showed a volcano shape, which indicates Lewis acid with moderate strength led to high yield of HCPN. Based on the above results, it is reasonable to conclude that metal oxides with moderate Lewis acidity are effective for the aldol condensation and dehydration for the ring rearrangement reaction, and enhance the yield of HCPN.

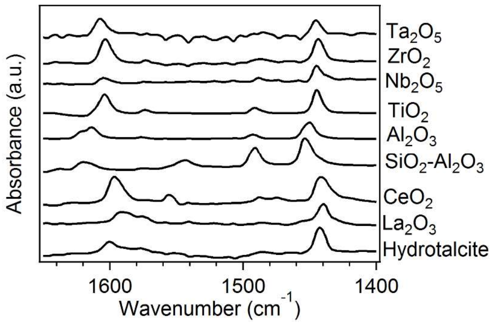


Fig. 3. FT-IR spectra of pyridine adsorbed on the metal oxides.

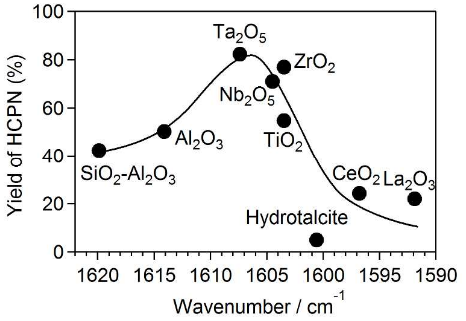


Fig. 4. Plot of the HCPN yields (Fig. 1) against the peak wavenumbers of adsorbed pyridine (ν_{8a}) at around 1610 cm^{-1} (Fig. 3).

Conclusions

In summary, we investigated the effect of heterogeneous acid-base catalysis on the conversion of HMF to HCPN using various acid-base metal oxides in combination with Pt/SiO_2. The reaction with the acidic metal oxides, in particular, Ta_2O_5, significantly enhanced the yield of HCPN (82% by Ta_2O_5 + Pt/SiO_2), but the basic metal oxides or no metal oxides (only Pt/SiO_2) give low yield of HCPN (< 25%). The time course of the products indicated that the acidic metal oxides facilitate the intermediate steps involving aldol addition and dehydration. The FT-IR study suggested that the Lewis acid with moderate acid strength leads to high yield of HCPN. Based on the results, metal oxides with moderate Lewis acidity are effective for the conversion of HMF to HCPN because they facilitate the aldol addition and dehydration for the ring rearrangement reaction.

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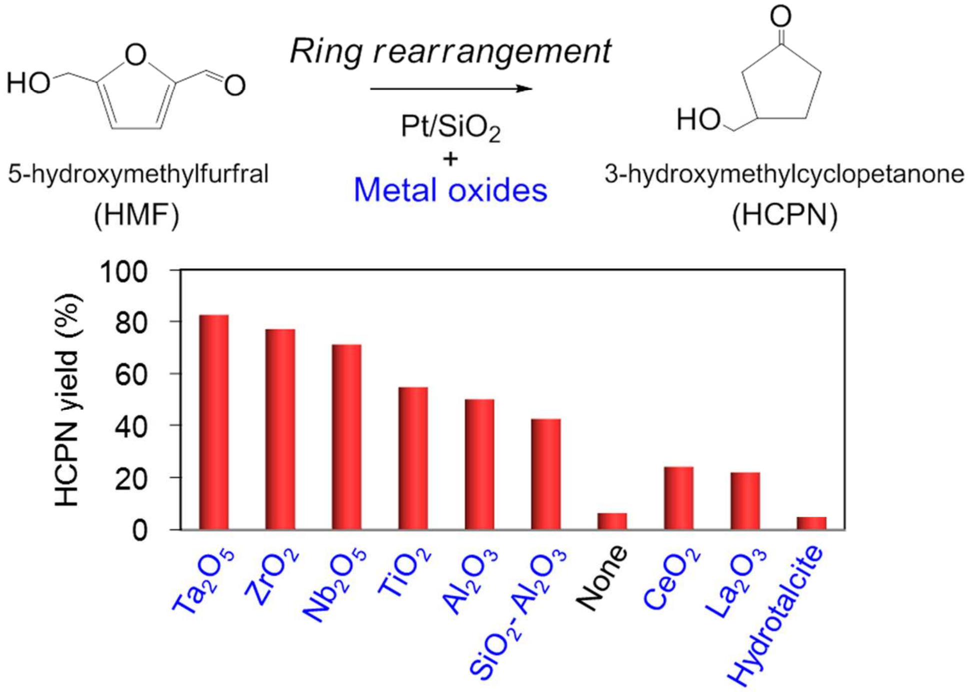

Acidic metal oxides, in particular, Ta_2O_5, significantly enhanced the conversion of 5-hydroxymethylfurfural to a cyclopentanone derivative.
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