[Review Paper]

Selective Oxidation of Biomass-derived Alcohols with Supported Metal Catalysts

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Simple transformation of sustainable biomass-resources to value-added chemicals and fuels has become important to diminish our heavy reliance on decreasing petroleum resources. Biomass-derived materials with hydroxyl groups such as 5-hydroxymethylfurfural (HMF) and glycerol can be obtained from sugars directly and transesterification of triglycerides with methanol as by-products, respectively. These chemicals are versatile starting materials because hydroxyl groups can be easily converted to afford value-added chemicals and fuels under oxidative/reductive conditions using supported metal catalysts. This review overviews recent studies on supported metal catalyzed oxidation reactions of HMF, glycerol and biomass-derived aliphatic α,ω -diols together with our research to develop highly efficient catalytic systems for bio-refining, based on petroleum conversion and nanotechnologies. Especially, role of external bases in the selective oxidation of biomass-derived alcohols will be discussed. We found that external base-free oxidation of HMF and glycerol is possible if basic supports are used. The activity of alloyed metal nanoparticles for selective oxidation of aliphatic α,ω -diols to ω -hydroxycarboxylic acids in basic aqueous media at high-pH value is also demonstrated.

Keywords5-Hydroxymethylfurfural, Glycerol, Aliphatic α,ω -diols, Selective oxidation, Supported metal catalyst, Bimetallic nanoparticle**1. Introduction**

Biomass is produced by photosynthesis from CO₂, H₂O, and sunlight, so can be considered as a renewable energy source in contrast to the limited resources of fossil fuels. Consequently, chemical transformations of biomass into energy sources and valuable chemicals are receiving much attention^{1)~7)}. Among such processes, conversions of sugars into valuable biomass-based compounds with hydroxyl groups^{8)~12)} are key chemical transformations because sugars can be obtained from cellulose and hemicellulose, the main components of wood. For example, 5-hydroxymethylfurfural (HMF) can be produced from glucose and/or fructose⁸⁾, which is known as a key precursor for the synthesis of chemicals with many applications in the pharmaceutical and polymer industries. This review describes recent research on oxidative transformations of biomass-based alcohols such as HMF, glycerol and aliphatic α,ω -diols using supported metal catalysts.

2. Oxidative Transformations of HMF

The HMF molecule contains aldehyde and hydroxyl groups on a furan ring. Therefore, selective transformations of these two functional groups with conventional reactions such as oxidation, reduction, hydrogenolysis and condensation have been widely investigated to produce chemicals and fuels¹³⁾. For example, HMF-based diols of 2,5-bis(hydroxymethyl)furan (BHMF)^{14),15)} and 2,5-bis(hydroxymethyl)tetrahydrofuran (BHMTTHF)^{16),17)} are candidates for biomass-derived monomer sources. HMF can also be oxidized into 2,5-diformylfuran (DFF) and/or 2,5-furandicarboxylic acid (FDCA) (**Scheme 1**). FDCA is a possible candidate monomer for terephthalic acid, a precursor of terephthalate polymers. Zhang and Deng reviewed recent methods for synthesis of FDCA from HMF, with special attention to catalytic systems, mechanistic insights, reaction pathways, and catalyst stability¹⁸⁾. Here, recent research on the synthesis of FDCA and DFF by oxidation of HMF using heterogeneous catalysts with or without addition of external bases is introduced.

Various metals such as platinum, palladium or gold are known to catalyze oxidation of HMF into FDCA

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Scheme 1 Oxidative Transformations of HMF

using molecular oxygen as the oxidant¹⁸). For example, Sahu and Dhepe compared the catalytic performance of various metal-oxide supported Pt catalysts with 0.1 MPa O₂ in the presence of NaOH (1 equiv.) at 348 K for 12 h¹⁹). Under the same reaction conditions, Pt/ γ -Al₂O₃, Pt/ZrO₂, and Pt/C showed high catalytic activity with FDCA yields of 96, 94, and 89 %, respectively. In contrast, Pt supported on reducible TiO₂ and CeO₂ produced little FDCA (2 % and 8 % yields) even with *ca.* 100 % HMF conversion. Cai *et al.* reported superior catalytic performance of Au nanoparticles (1 nm size) encapsulated in the supercage of HY zeolite for selective HMF oxidation into FDCA with > 99 % FDCA yield in water under 0.3 MPa O₂ in the presence of NaOH at 333 K²⁰). It has been reported the structures of Au nanoparticles and HY zeolite are stable under these conditions, and the Au/HY catalyst is reusable for several catalytic cycles. Negatively-charged Au nanoparticles may be responsible for this excellent catalytic performance.

Pasini *et al.* reported AuCu bimetallic alloy catalyst (4.4 nm diameter) supported on TiO₂ for HMF oxidation to FDCA under 1 MPa O₂ in the presence of NaOH at 368 K to afford 99 % FDCA yield with complete HMF conversion²¹). A strong synergistic effect is evident with the addition of Cu to Au, especially for catalyst reusability without significant leaching of metal nanoparticles. However, stability test experiments showed the final product is mainly 5-hydroxymethyl-2-furancarboxylic acid (HMFA) instead of FDCA. Reusable Pd-modified Au/carbon (Au₈Pd₂/C) catalyst has been developed for HMF oxidation to FDCA under 3 MPa O₂ in the presence of NaOH at 333 K, giving 99 % FDCA yield with complete HMF conversion²²).

The mechanism of HMF oxidation over Au and Pt catalysts at high pH has been investigated using isotopically labeled O₂ and water²³). It was shown that the source of oxygen insertion is H₂O rather than O₂.

The HMF oxidation is initiated by rapid, reversible hydration of the aldehyde moiety to form a geminal diol intermediate *via* nucleophilic addition of water to the carbonyl moiety. It was proposed that O₂ acts as a hydride scavenger from the metal catalyst surface to complete the catalytic cycle, releasing water. The OH⁻ anion could facilitate formation of the metal-alkoxide intermediate from alcohol *via* proton abstraction²⁴) and dehydrogenation of the geminal diol intermediate to afford the carboxylic acid.

HMF oxidation at high pH is economically and environmentally unfavorable, leading to development of “external base-free” HMF oxidation using solid catalysts. Layered Mg–Al mixed hydroxides or hydroxalicates (HTs)²⁵) have hydrophilic surface base sites originating from HCO₃⁻ species, which are not poisoned by exposure to air (CO₂ and H₂O) unlike MgO and CaO activated at high temperatures²⁶). Therefore, HTs can act as a heterogeneous base catalyst even in water solvent²⁷) and used as a metal support²⁸)~⁴¹). The most important character of HTs as a metal support is the surface basicity which promotes the abstraction of protons from organic molecules, especially from alcohols even after metal immobilization. This concept could be applied to Au-catalyzed base-free HMF oxidation using basic HT as a support.

Our research group used a 1.9 wt% Au/HT catalyst with Mg/Al ratio of 5 for the aqueous oxidation of HMF at 368 K with 0.1 MPa O₂ for 7 h without addition of any external base (HMF/metal = 40 mol/mol) (Scheme 2)³²). The Au/HT efficiently catalyzed HMF oxidation to form FDCA with 99 % selectivity with complete HMF conversion. The Au/HT catalyst could be reused at least three times without significant loss of activity. X-ray absorption near edge structure (XANES) and transmission electron microscope (TEM) measurements showed no changes in the gold oxidation state, morphology and particle size (3.2 nm) of the reused Au/

Scheme 2 Oxidation of HMF by Au/HT and Ru/HT Catalysts without External Base^{32),41)}

HT catalyst. Some other research groups also tried to use Au/HT catalyst with different Mg/Al ratio for base-free HMF oxidation under different reaction conditions^{42),43)}, but found leaching of the HT during the reaction. The basicity, crystallinity and stability of the HT strongly depends on the Mg/Al ratio and the preparation method³¹⁾. Indeed, Wilson *et al.* employed a unique alkali-free method for the preparation of HT^{43),44)}. Under severe reaction conditions, the HT may dissolve into the reaction medium that contains the carboxylic acid FDCA⁴²⁾. For Au/HT catalyst, addition of external base could also accelerate HMF oxidation to FDCA^{43),45)}.

Selective oxidation of HMF into FDCA under external base-free conditions is possible. Actually, Siankevich and co-workers reported poly(vinylpyrrolidone) (PVP)-stabilized Pt nanoparticles (Pt-PVP) for the base-free aerobic oxidation of HMF in water at 353 K after 24 h with 0.1 MPa O₂ formed FDCA with 95 % yield and 100 % HMF conversion⁴⁶⁾. The Pt-PVP catalyst showed slightly decreased activity in the recycling runs. Isotope labeling experiments revealed the mechanism of base-free oxidation of HMF into FDCA over PVP-stabilized Pd nanoparticles catalyst in H₂¹⁸O for 4 h. The release of 2H⁺ from the hydroxyl group in HMF generated DFF intermediate. Mass spectrometric analysis of the reaction mixture revealed FDCA incorporated 4 and 3 ¹⁸O atoms. The aldehyde group may also undergo rapid reversible hydration to a geminal diol *via* nucleophilic addition of water to the carbonyl and subsequent proton transfer to metal nanoparticles. Subsequently, 2H is transferred to the surface of the metal, generating the carboxylic groups. Molecular oxygen reacts with the surface hydride to release H₂O to complete the catalytic cycle even under base-free conditions. The same mechanism was proposed for base-free aqueous HMF oxidation using Pt/active carbon catalyst and H₂¹⁸O⁴⁷⁾.

Wang *et al.* reported a stable and efficient carbon nanotube (CNT)-supported AuPd alloy catalyst for the aerobic oxidation of HMF to FDCA in water without added bases, in which support-enhanced adsorption and the alloying effects are essential in the oxidation⁴⁸⁾. Functionalized CNT provides efficient support of Pt

nanoparticles (3.3 nm) for external base-free HMF oxidation into FDCA⁴⁹⁾. The carbonyl/quinone and/or phenol groups on CNT surfaces are crucial in the enhancement of HMF adsorption as well as reaction intermediates from the water phase which might facilitate hydrogen transfer. Han *et al.* also realized base-free aerobic oxidation of HMF to FDCA using a novel Pt/C-O-Mg catalyst for ten cycles with little loss of activity⁵⁰⁾. The C-O-Mg support contained strong and stable basic sites. The C-O-Mg material was prepared by hydrothermal treatment of a mixture of MgO and resorcinol (1,3-dihydroxybenzene) at 453 K, followed by heating in a N₂ flow at 1027 K and treatment with excess HCl (1 mol L⁻¹) at room temperature. The final treatment was carried out to remove free MgO from the obtained carbonated material. The C-O-Mg has an amorphous carbon phase and a high specific surface area (1220 m² g⁻¹). A scale-up experiment was successfully performed with this catalytic system to afford FDCA with 75 % isolated yield and 99.5 % purity.

N-doped carbon supported Pt catalyst, prepared *via* the hydrothermal method using glucose and resorcinol as carbon sources and ethylenediamine as a nitrogen source, promotes HMF oxidation under base-free aqueous solution to afford FDCA with 96 % yield at 383 K for 12 h⁵¹⁾. Several types of nitrogen were introduced into the carbon structure as detected by X-ray photoelectron spectroscopy (XPS). The basicity of N-doped carbon was evidenced by CO₂-temperature-programmed desorption (TPD), which suggests that involving N in catalyst preparation generates new medium strength base sites on the support surface. Decrease of the catalytic activity was observed due to the slight leaching of Pt and N, and the growth of Pt nanoparticles during the recycling procedures.

The choice of metal species could control the product selectivity of HMF oxidation. Using Ru as the active center, the main product of aerobic HMF oxidation in *N,N*-dimethylformamide (DMF) solvent is DFF (Scheme 2)⁴¹⁾. In this oxidation, basic HT is a superior support. High selectivity for DFF could be ascribed to the low activity of Ru species for the oxidation of the aldehyde moiety to carboxylic acids²⁴⁾. Antonyraj *et al.* reported total HMF conversion with 97 % DFF selectivity at 403 K under 0.28 MPa O₂ after 4 h was achieved using Ru/ γ -Al₂O₃ catalyst in toluene solvent⁵²⁾. Trimetallic mixed oxide RuCo(OH)₂CeO₂, which is active for aerobic oxidation of primary alcohols⁵³⁾, catalyzed HMF oxidation to DFF with 83 % yield at 97 % HMF conversion at 393 K in methyl isobutyl ketone solvent after 12 h⁵⁴⁾. Wang *et al.* reported [Fe₃O₄@SiO₂-NH₂-Ru^{III}] catalyst for the HMF oxidation to DFF in toluene solvent⁵⁵⁾. The catalyst was magnetically separable and could be reused several times. Covalent triazine frameworks (CTF)-supported Ru cluster species catalyzed HMF oxidation to DFF at

Reaction conditions: HMF (1 mmol), Ru/FeHT (0.1 g), DMF (3 mL), O₂ flow (20 mL min⁻¹), 373 K, 6 h.

Fig. 1 Yield of DFF and Photograph of Magnetic Separation after 4 Reaction Cycles

353 K under 2 MPa air in methyl *t*-butyl ether solvent⁵⁶. CTF support is superior to activated carbon, γ -Al₂O₃, HT or MgO under those reaction conditions. A reusable Ru^{III}-incorporated zirconium phosphate catalyst could oxidize HMF in *p*-chlorotoluene solvent at 383 K with 0.1 MPa O₂ to afford DFF as the main product⁵⁷.

Magnetic separation of the catalyst is an interesting approach to reduce the energy requirement for filtration and centrifugation in the batch reactor after the reaction⁵⁸. Ru-stabilized magnetically separable HT catalyst was prepared by adsorption of RuCl₂ aq. onto FeHT⁵⁹, and applied for both selective oxidation of HMF to DFF and one-pot synthesis of DFF from fructose. The actual metal loadings of Ru: 3.7 wt% and Fe: 1.5 wt% were estimated by ICP-AES analysis. As shown in **Fig. 1**, the yields of DFF were 72, 65, 57 and 57 % with high selectivity (> 94 %) for 1-4th runs, respectively. The used catalyst was easily separated by a Nd magnet (*ca.* 460 mT) after 4 cycle reactions. One-pot synthesis of DFF *via* dehydration of fructose to HMF over Amberlyst-15 and successive oxidation of HMF to DFF provided 48 % yield with effective separation of the magnetic Ru/FeHT catalyst from the acid-resin Amberlyst-15 catalyst (**Fig. 2**)⁶⁰.

3. Oxidative Transformations of Glycerol

Glycerol (1,2,3-propanetriol) is one of the by-products from the biodiesel industry process of base-catalyzed transesterification of triglycerides with methanol^{42),61)~63}. Consequently, glycerol has been produced in large quantities with the increase in biodiesel production. Therefore, research on uses for glycerol has been encouraged^{62)~65}. Glycerol contains three hydroxyl groups (one secondary and two primary hydroxyl

Fig. 2 Magnetic Separation in the Reaction Mixture in the Presence of Amberlyst-15 and Ru/FeHT Catalyst in One-pot Synthesis of DFF from Fructose⁶⁰

groups), so glycerol is a potential starting material for several highly valuable fine chemicals important in the food, cosmetics, and pharmaceutical industries through chemical reactions such as oxidation, hydrogenolysis and dehydration⁶². Recent research in the field of selective oxidation of glycerol using supported metal catalysts as well as our recent research topics are described here.

Oxidation of glycerol is generally catalyzed by various metals such as palladium, platinum, bismuth or gold, and results in a wide range of products as shown in **Scheme 3**. The product selectivity depends on the type of the active metal, but is also influenced by many parameters such as the metal particle size, pore size of the support and the pH of the reaction medium^{42),66}.

Supported metal nanoparticles were frequently utilized for the oxidation of glycerol⁶². Aqueous oxida-

Scheme 3 Oxidative Transformations of Glycerol

tion of glycerol in the presence of NaOH, Au, Pt, and Pd nanoparticles supported on carbon-based materials generally forms glyceric acid as a major product⁶³.

Carbon materials with regular spherical-shaped and uniform size distribution (100–125 μm) have been used as a support for Pt nanoparticles (less than 10 nm diameter). The resulting catalysts showed activity for the oxidation of glycerol at 343 K under 1 MPa O_2 in the presence of NaOH to afford glyceric acid with 82 % selectivity at 66 % glycerol conversion⁶⁷.

Well-dispersed AuPd nanoparticles (1.0–3.0 nm) stabilized in a commercial anion-exchange resin (Amberlite IRA402BLCL) showed stable catalytic activity (> 4000 min) for liquid-phase glycerol oxidation in the presence of NaOH with a fixed bed flow type reactor and 0.1 MPa O_2 at 333 K with conversion of *ca.* 50 %, and selectivity of *ca.* 60 % and 30 % for glyceric and tartronic acids, respectively⁶⁸. Recently, Jin *et al.* reported Co/Mg–Al catalyst prepared by sol-gel method was found to be active for aqueous glycerol oxidation at 343 K with 0.1 MPa O_2 and NaOH, forming tartronic acid with 64 % selectivity at 100 % glycerol conversion⁶⁹. The Co species concentrated on the Mg_3AlO_x surface were proposed to catalyze this deep glycerol oxidation.

The action of the base, hydroxide ions, is to abstract the proton of alcohols as the first step of the dehydrogenation pathway to form metal-alkoxide intermediate species. Zope *et al.* demonstrated that oxygen atoms originating from hydroxide ions are incorporated into the alcohol, not from the O_2 atmosphere, using labeling experiments with $^{18}\text{O}_2$ and H_2^{18}O for glycerol oxidation on supported Au catalysts⁷⁰.

The major challenge associated with the selective oxidation of glycerol is to minimize the usage of alkali external bases. Therefore, base-free oxidation of glycerol has been attempted using AuPt nanoparticles sup-

ported on TiO_2 , MgO and H-mordenite with different acid-base properties at 353 K, resulting in glyceric acid as the main product in most cases^{63,71,72}. Base-free oxidation of glycerol in water is also possible at 293 K with 0.1 MPa O_2 using hydrotalcite (HT)-supported gold nanoparticle catalysts, which were synthesized by simple deposition-precipitation and successive calcination³³. Au/HT was found to transform glycerol to glycolic acid (hydroxyacetic acid, selectivity; 53 %) through C–C bond cleavage (Scheme 3). XANES revealed that calcination of Au/HT at temperatures higher than 373 K afforded reduced Au^0 species, which are catalytically active sites. Such bare Au/HT catalysts were applicable for the aerobic oxidation of glucosamine-HCl into α -amino acid³⁵ and sugars into sugar acids in water³⁶. External base-free selective glycerol oxidation in water solvent with 0.1 MPa O_2 was also demonstrated by using Pt/HT catalysts under mild conditions (333 K)³⁴. Pt/HT catalyst, with Pt particles of 2 nm diameter, showed high activity to form glyceric acid with selectivity of 78 %, even at high glycerol/metal molar ratios of up to 3125. This catalytic activity was attributed to careful control of the Pt^0 concentration and basicity of the support.

Ligands could control the catalytic activity of metal nanoparticles *via* coordination to metal particle surface⁷³. We prepared HT-supported ligand-stabilized monometallic platinum nanoparticles by the immobilization method with soluble starch as a reducing and stabilizing agent (Pt-starch/HT), and applied the catalysts to the oxidation of glycerol with 0.1 MPa O_2 as oxidant in water at 323 K without adding external base³⁸. After 6 h, the conversion of glycerol to glyceric acid reached 63 % with 68 % selectivity. The catalyst was removed from the solution by simple filtration after the reaction and could be reused up to three times with high selectivity (71 % in the third cycle). Presumably some

Scheme 4 Aerobic Oxidation of 1,2-Propanediol by Pt₆₀Au₄₀-starch/HT Catalyst³⁹⁾

part of the starch polymer structure covered the surface of the Pt nanoparticles and limited oxygen diffusion, thus controlling over-oxidation to C1 products, resulting in the high selectivity for glyceric acid on Pt-starch/HT catalyst. The action of starch as stabilizing ligand in the oxidation of polyols has been investigated in comparison with conventional ligands such as PVP and poly(vinyl alcohol) (PVA)⁴⁰⁾. The particle size of the supported Pt nanoparticles was controlled to *ca.* 2.2 nm by changing the polymer amount during the preparation of Pt nanoparticles, eliminating the size effect of the particles. Starch was an effective ligand for stabilized Pt nanoparticles, which preserved the abundance of negatively charged to active surface and provided suitable wettability for water solvent (hydrophilicity, evaluated by contact angle measurement). Such properties resulted in the high catalytic activity of Pt-starch/HT for external base-free aqueous oxidation of 1,2-propanediol into lactic acid at 298 K. The Pt-starch/HT catalyst was little dispersed in nonpolar solvents such as toluene, although bare Pt/HT could be dispersed. Affinity for the solvent may be strongly related to the dispersibility of the catalyst, and can be influenced by capping agents.

Bimetallic Pt₆₀Au₄₀-starch/HT catalyst at 298 K for 6 h in water solvent with 0.1 MPa O₂ converted glycerol into glyceric acid with 73 % yield and 78 % selectivity³⁹⁾. This catalytic system can be applied for the oxidation of 1,2-propanediol, which contains one primary OH and one secondary OH group, into lactic acid (Scheme 4). In our catalytic system, the primary OH groups of aliphatic polyols are selectively oxidized to the corresponding monocarboxylic acids.

Tomishige *et al.* reported base-free glycerol oxidation using PdAg alloy particle catalyst supported on carbon with 0.3 MPa O₂ at 323 K for 4 h converted glycerol to dihydroxyacetone with 82 % selectivity under less than 10 % conversion⁷⁴⁾. The mechanism may involve the terminal OH group of glycerol adsorbed on the Ag site and the neighboring secondary OH group (CH-OH) attacked by the oxygen species dissociatively adsorbed on the Pd site.

Chen *et al.* reported oxidation of glycerol over reusable Pt catalysts supported on nitrogen-doped carbon nanotubes (Pt/N-CNTs) with 0.1 MPa O₂ at 333 K in base-free aqueous solution formed glyceric acid with 43 % selectivity and 51 % conversion⁷⁵⁾. TPD analyses indicated that the surface of the CNTs had basic sites originating from doped nitrogen atoms.

Formic acid (HCO₂H), an important commodity chemical as well as a promising medium for hydrogen storage and hydrogen production, can be obtained from highly concentrated aqueous glycerol solution using vanadium-substituted phosphomolybdic acids as catalysts and O₂ as oxidant; 3.64 g of formic acid was produced from 10 g of glycerol/water (50/50 in weight) solution⁷⁶⁾. Formic acid can be also obtained from various monosaccharides directly using solid acid-base catalysts and aqueous hydrogen peroxide as an oxidant^{77),78)}.

4. Oxidative Transformations of Biomass-based Aliphatic α,ω -diols

Biomass-based diols can be directly applied to industrial applications for the synthesis of important polymers and further chemical transformations as well as conventional petroleum-based diol chemistry^{79)~81)}. Especially, the synthesis of biomass-based aliphatic α,ω -diols such as ethylene glycol (C2) from glucose, 1,3-propanediol (C3) from glycerol, 1,4-butanediol (C4) from succinic acid, 1,5-pentanediol (C5) from furfural, and 1,6-hexanediol (C6) from HMF have been widely examined.

One of the important catalytic transformations of aliphatic α,ω -diols is lactonization. Lactones have considerable uses as liquid fuels, solvents, and organic intermediates in the synthesis of fine chemicals for applications such as flavors and medicines. Kaneda and co-workers surveyed a wide range of α,ω -diols can be converted to the corresponding lactones in high yield over Au/HT in toluene (oxidation reaction)⁸²⁾ and Cu/HT in mesitylene (dehydrogenation reaction)⁸³⁾. For instance, 1,4-butanediol and 1,5-pentanediol gave the corresponding γ -butyrolactone and δ -valerolactone in high yields (83-99 %) with high selectivity (> 96 %). Aerobic oxidation of α,ω -diols to lactones was also reported for Au/ γ -Al₂O₃ in tributyl phosphate⁸⁴⁾ or Au/anion-exchange resin in toluene⁸⁵⁾.

In this section, we focused on the selective oxidation of α,ω -diols in water. Water acts as the nucleophilic agent to form lactones and polylactones, so different types of products, ω -hydroxycarboxylic acid and/or α,ω -dicarboxylic acids, can be expected. Especially, the bifunctionality of ω -hydroxycarboxylic acid allowed conversion into a broad range of valuable new building blocks for organic synthesis and high performance polymers^{86)~88)}.

4.1. Synthesis of 3-Hydroxypropionic Acid with Selective Oxidation of 1,3-Propanediol

We examined the selective oxidation of 1,3-propanediol (1,3-PD, C3) to 3-hydroxypropionic acid (3-HPA) over bimetallic AuPd catalyst based on our previous experiences with aerobic aromatic alcohol oxidation using the highly active PVP-capped AuPd/HT catalyst^{37),89),90)}. 1,3-PD can usually be obtained from the selective

Table 1 Aerobic Oxidation of 1,3-PD to 3-HPA over AuPd-PVP/HT in Water^{93),a)}

Catalyst ^{c)} (average particle size)	Conversion [%]	Yield [%]		TON ^{d)}
		3-HPA	MA	
Au ₁₀₀ -PVP/HT (agglomerates)	1	0	0	0
Au ₈₀ Pd ₂₀ -PVP/HT (3.1 nm)	45	30	3	43
Au ₆₅ Pd ₃₅ -PVP/HT (2.5 nm)	58, 37 ^{b)}	42, 32 ^{b)}	10, 5 ^{b)}	69, 105 ^{b)}
Au ₄₂ Pd ₅₈ -PVP/HT (2.5 nm)	67	32	18	44
Au ₂₃ Pd ₇₈ -PVP/HT (2.6 nm)	76	20	24	19
Au ₉ Pd ₉₁ -PVP/HT (2.7 nm)	61	18	14	14
Pd ₁₀₀ -PVP/HT (2.6 nm)	17	15	0	10
Au/HT (3.3 nm)	36	30	6	59

a) Reaction conditions: 1,3-PD (1.0 mmol), H₂O (7.5 mL), catalyst (0.1 g, 0.05 g^{b)}), O₂ flow (10 mL min⁻¹), 343 K, 12 h. c) Au/Pd ratio and d) TON value were determined by the actual amount of Au and Pd loadings determined by ICP-AES.

hydrogenation of glycerol, a waste biomass resource^{91),92)}. Our findings for the aerobic oxidation of 1,3-PD over as-prepared AuPd-PVP/HT in water are shown in **Table 1**. Among the monometallic catalysts, Au₁₀₀-PVP/HT (Au agglomerates) was inactive (0 % yield) but bare Au/HT (3.3 nm Au nanoparticles) was fairly active (30 % yield), whereas Pd₁₀₀-PVP/HT (2.6 nm Pd nanoparticles) gave only 15 % yield. Accordingly, the nano-sized Au sites may be the major active center for the oxidation reaction in water. Addition of Pd to Au nanoparticles seemed to increase the conversion of 1,3-PD, whereas the yield for 3-HPA was the highest at 42 % using 35 atm% Pd loading in Au nanoparticles. The Au₆₅Pd₃₅-PVP/HT catalyst was reusable and exhibited a TON value of 105 with 32 % yield and 86 % selectivity for 3-HPA production⁹³⁾. The bimetallic AuPd-PVP/HT catalyst had achieved significantly high TON value (= 395,700) for conventional aromatic alcohol oxidation of 1-phenylethanol to acetophenone³⁷⁾. However, surprisingly, selective α,ω -diol oxidation to α -hydroxyl acid in water without homogeneous base agent seems to demand more highly focused strategy in the nano-structured active centers and/or catalytic system, even such a novel oxidation catalyst.

As a pioneer work, Behr *et al.* patented oxidation of 1,3-PD in an aqueous alkaline solution in the presence of Pd containing catalyst⁹⁴⁾. Trimetal Pd₅₆Pt₈Bi₃₆-supported active carbon showed the highest 82 % yield for production of the alkali metal salt of 3-HPA. 1,3-

PD oxidation in methanol solvent has been reported, but formation of 3-HPA scarcely occurred because methyl 3-hydroxypropionate is the major product due to oxidative esterification^{95)~97)}.

Oxidation of allyl alcohol (ALA), which can be obtained from both biomass-based glycerol and petroleum-based propene, is another route for 3-HPA production (**Scheme 5**). Yang *et al.* investigated ALA oxidation over Au/CeO₂ in basic aqueous solution giving 51 % yield for 3-HPA formation under 0.3 MPa O₂⁹⁸⁾. ALA was little converted, and no by-products were detected, in the absence of NaOH. Pina *et al.* studied the effect of NaOH agent on the oxidation of ALA in water with as-prepared Au/C and pressurized O₂ (0.3 MPa) found that high selectivity at full conversion to the desired 3-HPA (79 % yield) could be achieved using excess NaOH (NaOL/ALA = 3 molar ratio) at 323 K, because the Au/C was not stable and the selectivity to 3-HPA was decreased after the second reaction cycle due to Au aggregation⁹⁹⁾. Further investigation of the glucose-capped bimetallic AuM/C (M = Pd, Pt, Cu or Ag) catalytic system by the same group found Au₉₉Cu/C prepared *via* the co-reduction method gave selectivity of 95 % for 3-HPA production in the 1st run, and retained high selectivity (*ca.* > 75 %) up to the 7th run¹⁰⁰⁾. Unfortunately, both activity and selectivity decreased remarkably after the 8th run. The low redox potential of Cu may be implicated in such sustained high performance. Formation of 3-HPA in the hydra-

Scheme 5 Schematic Route for 3-HPA Production

Scheme 6 Schematic Route for 6-HHA Production

tion of acrylic acid is known¹⁰¹), obtained by the dehydration of lactic acid or levulinic acid¹⁰²) formed by HMF hydration.

4.2. Synthesis of 6-Hydroxyhexanoic Acid with Selective Oxidation of 1,6-Hexanediol

1,6-Hexanediol (1,6-HD) can be obtained from biomass by selective C–O hydrogenolysis in the ring of HMF^{81),103),104)}. Oxidation of 1,6-HD to 6-hydroxyhexanoic acid (6-HHA) in water was examined using AuPd bimetallic catalyst prepared with three different capping agents under aqueous basic media in a Schlenk flask reactor. The capping agent had a major effect on the formation mechanism and/or catalysis of metal nanoparticles^{105)–109)}. Therefore, we considered that the combination of controlled AuPd active center induced by different capping agents and basic media, which is well-known as an accelerator for oxidation reaction, could lead a breakthrough in the challenging selective aerobic oxidation reaction of aliphatic α,ω -diol. The schematic route for 6-HHA production is shown in

Scheme 6. Conventionally, 6-HHA is produced *via* the reduction of adipic acid^{110),111)}, obtained from oxidation of petroleum-based cyclohexane^{112),113)}.

Figure 3 shows the 1,6-HDO oxidation in water over PVP, PVA or DDAO-capped AuPd/HT catalyst, prepared with the ethylene glycol reduction method (Au/Pd = 40/60 molar ratio, in theory). The reactants were acidified by H₂SO₄ aq. before high performance liquid chromatography (HPLC) analysis in all experiments. The conversion was high (85–95 %) in all cases, whereas the distribution of products seemed to depend on the capping agent. The yield for HHA was DDAO (81 %) $\gg$ PVA (61 %) $>$ PVP (58 %) whereas the yield for AA was PVP (29 %) $>$ PVA (19 %) $\gg$ DDAO (4 %). The actual metal loadings of Au and Pd (inductively coupled plasma-atomic emission spectroscopy, ICP-AES) indicated that the TON value for HHA formation (Au/Pd composition) was 372 (Au₃₆Pd₆₄-PVA/HT) $\gg$ 180 (Au₃₈Pd₆₂-DDAO/HT) $>$ 123 (Au₃₉Pd₆₁-PVP/HT), but significantly higher selectivity towards

Reaction conditions: 1,6-HDO (0.5 mmol), catalyst (25 mg), H_2O_2 (6 mmol), NaOH (0.375 mmol), H_2O (5 mL), 353 K, 8 h.

Fig. 3 Results of 1,6-HDO Oxidation in Water over PVP, PVA or DDAO-capped AuPd/HT Catalyst¹¹⁸⁾

Reaction conditions: 1,6-HDO (0.5 mmol), catalyst (25 mg), H_2O_2 (6 mmol), NaOH (0.375 mmol), H_2O (5 mL), 353 K.

Fig. 4 Time-course over Au₃₈Pd₆₂-DDAO/HT for 1,6-HDO Oxidation in Water

HHA formation was observed only for Au₃₈Pd₆₂-DDAO/HT (93 %). The largest TON for HHA production was 265 on 5 mmol scale in the case of Au₃₈Pd₆₂-DDAO/HT (71 % yield, 91 % sel.¹¹⁴⁾. Such high activity for HHA production is rarely reported for α,ω -diol oxidation: 33 % yield on reactive iodine species¹¹⁵⁾, approximately 36 % yield on Pt/C¹¹⁶⁾ and 20 % on Pt₃Sn₁/C¹¹⁷⁾. The differences in reactivity ascribed to the type of capping agent used depend on the differences in both electronic state and nanostructure; *i.e.* DDAO-capped AuPd has core-shell structure and fewer negative Au atoms, whereas PVP and PVA-capped AuPd have homogeneous AuPd alloy and highly negative Au atoms¹¹⁸⁾.

The time course on Au₃₈Pd₆₂-DDAO/HT showed extraordinarily selective formation of 6-HHA through 1,6-HD conversion in water even after 24 h reaction, as shown in Fig. 4. AA formation was negligible

(< 10 %), and no aldehyde intermediates were detected. Additionally, H_2O_2 completely disappeared at the 20 min reaction as determined by iodometric titration, so the rate of H_2O_2 decomposition was independent of diol oxidation. It is said that H_2O_2 decomposition is favored by alkali^{119),120)}. According to these results, the reaction might proceed on the basis not of a hydroxyl radical mechanism such as Fenton^{121),122)} but an O_2 molecular-mediated mechanism^{123)~125)}. In fact, O_2 flow (without H_2O_2) afforded 48 % yield whereas N_2 flow was inactive for 6-HHA production under the same reaction conditions. Notably, Davis *et al.* found out that O-insertion in acidic products occurs through H_2O molecules: water was the source of the oxygen atoms incorporated into the acid product, during oxidation of glycerol (to glyceric acid) and ethanol (to acetic acid) in the aqueous phase at high pH conditions as demonstrated by labeling experiments with $^{18}\text{O}_2$ and H_2^{18}O ⁷⁰⁾. We supposed a similar reaction mechanism would occur in our reaction system. AuPd-DDAO/HT catalyzed highly selective oxidations of α,ω -diols to ω -hydroxycarboxylic acids and was also applicable for C6-C8 diols¹¹⁸⁾, which are enormously valuable in polymer and resin production⁸⁸⁾.

The chemistry of aerobic oxidation in water at high pH is very important. Prati and Rossi studied the aerobic oxidation of vicinal diol over Au catalyst in water under strong alkaline conditions and indicated that ethylene glycol oxidation (to glycolic acid) occurred *via* the intermolecular Cannizzaro reaction or stepwise oxidation of a single alcohol functional group (Scheme 7)¹²⁶⁾. Glycolate (lactic acid) is stable under basic conditions, whereas glyoxal (oxalaldehyde) or glyoxylate (2-oxoacetic acid) undergo only the Cannizzaro reaction. Interestingly, Au/C was inactive for further oxidation of glycolic acid to oxalic acid though Pd/C and Pt/C showed slight activities. Moreover, the intermolecular Cannizzaro reaction also influenced the stability of aldehyde intermediates in the 1,2-propanediol oxidation and controlled the selectivity toward lactic acid production rather than pyruvic acid from pyruvic aldehyde under strong basic conditions (Scheme 8). Hibbitts *et al.* and Gangwal *et al.* proposed that a formation of geminal diol intermediate *via* nucleophilic addition of hydroxyl ions (OH^-) on the intermediate aldehyde may occur under high pH in water, and can subsequently dehydrogenate to form the corresponding acid product^{127),128)}. These reports agreed well with our observations; *i.e.* no aldehyde intermediates were detected in all stages.

Ide and Davis have carefully studied of the kinetics of aerobic α,ω -diol oxidation to α,ω -diacid over Pt/C under acidic conditions and found that a sequential reaction *via* aldehyde intermediates (*ex.* 6-hydroxyhexanal) was detected under acidic conditions¹¹⁶⁾. Oxidation of 1,6-HDO was about 4-5 times faster than

Scheme 7 Reaction Scheme for Ethylene Glycol Oxidation under Alkaline Condition

Scheme 8 Reaction Scheme for 1,2-Propanediol Oxidation under Alkaline Condition

oxidation of 6-HHA. We found that the rate was about 5 times faster over AuPd-DDAO/HT: 87 % conv. of 1,6-HDO with 81 % for 5-HHA yield and 25 % conv. of 5-HHA with 16 % yield for AA, respectively¹¹⁸. However, if 6-HHA was obtained as the intermediate species during transformation of 1,6-HDO to adipic acid, such a differential between the rate constants for the former and the latter reactions could not attain such a significantly high yield for intermediate^{129,130}; *i.e.* 3-HHA (81 %). The proximity of an electron-withdrawing group such as $-\text{OH}$ or $-\text{COOH}$ seemed to have little influence on the rate of oxidation because of the long chain length in the case of C6 alcohol. The presence of different functional groups, $-\text{OH}$ and $-\text{COOH}$, in the reaction mixture could be important in the adsorption step onto the active site and/or pH value in the media. These are still unresolved issues and need further investigations on the oxidation of ω -hydroxycarboxylic acid to α,ω -dicarboxylic acid under basic aqueous conditions. Very recently, we found an interesting report illustrating the simple preparation of highly pure monomeric ω -hydroxycarboxylic acids through saponification followed by H_2SO_4 acidification,

which afforded C6-C15 of ω -hydroxycarboxylic acids from their corresponding lactones in 80-85 % yield with > 99.5 % purity¹³¹. Elucidation of the competitive two formation paths: i) direct selective oxidation/acidification and ii) multi-step reactions of oxidative lactonization and successive saponification/acidification, is an important research topic for our future studies.

5. Conclusions

This review demonstrated the importance of supported metal catalyzed processes in selective oxidative transformations of biomass-based alcohols such as HMF, glycerol and aliphatic α,ω -diols into valuable chemicals. Basic conditions are important in the oxidation of HMF and glycerol, and oxidation reactions are possible under external base-free conditions if basic supports are employed for the active metal species. Therefore, novel techniques in catalyst design derived from petroleum chemistry would provide novel approaches in biomass transformation. Alloying with another metal species in the nano-scale is effective methodology to design highly functionalized heterogeneous catalysts

even for facile biomass conversions. We further demonstrated that the combination of recent nanotechnology (construction and analysis of active alloy centers) and classical theory (homogeneous base as an accelerating agent for oxidation) has identified interesting new catalytic behaviors in advanced oxidation reactions. Recently, facile transformations of new biomass-based targets such as bio-oil, hydrothermal liquefaction product of biomass^{132)~134)}, and shellfish biomass of chitin^{35),135~137)} are required for catalytic up-grading toward potential fuels and/or chemicals. Careful designs of metal active species and tuning of the acid-base property of the support through catalytic science, chemistry, and technology will improve the catalyst characteristics and help to establish a future sustainable society based on biomass-related materials.

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要 旨

金属担持触媒を用いたバイオマス由来アルコールの選択的酸化反応

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持続的な生産が可能なバイオマス由来資源から化成品・燃料を合成する触媒化学変換法は、持続可能な社会を実現する上で重要な技術の一つである。我々は、石油由来資源の変換プロセスで蓄積した触媒技術とナノテクノロジー研究での知見を生かし、金属担持触媒の調製とバイオマス由来資源から化成品・燃料を供給するプロセス技術の開発を行っている。本総合論文では、バイオマス由来の5-ヒドロキシメチルフルフラール

(HMF)、グリセロールおよび α,ω -ジオールをターゲット物質とした選択的酸化反応に関する我々の触媒開発プロセスと最近の動向を紹介する。HMFとグリセロールの選択的酸化反応では、塩基性担体を使用することで外部からの均一系塩基の添加を必要としない酸化反応を実現した。また、脂肪酸ジオール類の選択的酸化反応では、担持金属活性点のバイメタル化と反応系のpH制御が有効であることを明らかにした。