

# Reductive Conversion of 5-Hydroxymethylfurfural to 1,2,6-Hexanetriol in Water Solvent Using Supported Pt Catalysts

Hiroto Kataoka<sup>1</sup>, Daichi Kosuge<sup>1</sup>, Keiji Ogura<sup>1</sup>, Junya Ohyama<sup>1,2,3</sup>, and Atsushi Satsuma<sup>1,2\*</sup>

<sup>1</sup> Department of Materials Chemistry, Graduate school of Engineering, Nagoya University, Nagoya, 464-8603, Japan. <sup>2</sup> Elements Strategy Initiative for Catalysts and Batteries, Kyoto University, Kyoto, 615-8245, Japan. <sup>3</sup> Faculty of Advanced Science and Technology, Kumamoto University, Kumamoto, 860-8555, Japan. \*E-mail: satsuma@chembio.nagoya-u.ac.jp

One-pot conversion of biomass derived 5-hydroxymethylfurfural (HMF) to 1,2,6-hexanetriol (1,2,6-HT) in water solvent was performed using Pt catalysts supported on various acid-base metal oxides. Pt catalysts supported on hydrotalcite, MgO, and CeO<sub>2</sub> showed better yield of 1,2,6-HT and 2,5-bis(hydroxymethyl)-tetrahydrofuran (BHF), while ring-rearranged cyclopentanol derivatives were predominant products on the other Pt catalysts. The product distribution with time course on Pt/hydrotalcite revealed that HMF is at first hydrogenated to BHF, then the following parallel reactions proceed; ring-rearrangement to cyclopentanol derivatives, ring-hydrogenation to BHF, and hydrogenolysis to 1,2,6-HT. When pure hydrotalcite, MgO and CeO<sub>2</sub> were physically mixed with Pt/SiO<sub>2</sub>, the selectivity to 1,2,6-HT was almost zero or less than 10%. It was suggested that the formation of 1,2,6-HT proceeds at metal-support interface. The effect of metal-support interface was examined by means of IR spectra of adsorbed methanol. It was indicated that both basic property of supports and surface monodentate alkoxide formation are essential for the production of 1,2,6-HT. The maximum yield of 1,2,6-HT (42%) was obtained using Co-promoted Pt/CeO<sub>2</sub> catalysts pre-reduced at 200 °C.

**Keywords:** 5-Hydroxymethylfurfural, 1,2,6-Hexanetriol, Supported Pt Catalysts, Ring-opening reaction, Water Solvent

## 1. Introduction

Biomass derived 5-hydroxymethylfurfural (HMF) is known to be one of the key platforms of bio-refinery for production of various chemicals and fuels [1-5]. For examples, 2,5-bis-(hydroxymethyl)-furan (BHF) and 2,5-bis (hydroxymethyl)-tetrahydrofuran (BHTHF) can be obtained by hydrogenation of HMF and used as resin additives, solvents, feed stocks for polymers, drugs, and so on [6-12]. Oxidation of HMF produces 2,5-furandicarboxylic acid, which can be used as a monomer for engineering plastics [13]. Hydrogenolysis of HMF results in production of 2,5-dimethylfuran as a liquid fuel having high energy density. Straight chain alcohols and acids are also synthesized from HMF. 1,2,6-Hexanetriol (1,2,6-HT) is an intermediate for wetting agents, solvents, and pharmaceuticals, and is also used in the cosmetics and resin industries [14].

Since HMF is produced via hydrolysis of cellulose followed by isomerization and dehydration, selective conversion of HMF in water is advantageous in terms of energy saving and green chemistry [15]. However, compared to organic solvents, the selective conversion of HMF in water is difficult

because of interference of various side reactions; hydrolysis, ring rearrangement, and polymerization. However, there are some papers reporting selective conversion of HMF in water. Recently, our research group reported the selective conversion of HMF: Selective hydrogenation to BHF (96% yield) over Au nano-cluster supported on  $\text{Al}_2\text{O}_3$  [8], and one-pot hydrogenation and rearrangement of HMF to 3-hydroxymethylcyclopentanol (88% yield) [16]. For the conversion of HMF to straight-chain alcohols, two reaction pathways have been reported. One is two-step hydrogenation of HMF to BHTHF followed by hydrogenolysis to 1,2,6-HT. Buntara et al. selectively converted BHTHF to 1,2,6-HT at lower conversion level (Conv. 21%, Select. 97%,) using Rh-Re/ $\text{SiO}_2$  catalyst in water at 80 °C [17]. He et al. examined the selective production of 1,6-hexanediol from BHTHF via 1,2,6-HT. Using 10wt%Pt-10wt%WO<sub>x</sub>/ $\text{TiO}_2$  catalyst, consecutive production of 1,6-hexanediol via 1,2,6-HT proceeds when the catalyst amount was 0.50 g, while more than 95% selectivity of 1,2,6-HT was achieved with BHTHF conversion of 22% by use of 0.10 g catalyst in water [18].

Another pathway is direct one-pot conversion of HMF to diols or triol. Mizugaki et al. reported that Pt/hydrotalcite showed high performance for furfural conversion to 1,2-pentanediol (Conv. > 99%, Select. 73%) in 2-propanol [19]. In water solvent, Chen et al. reported that furfural conversion to 1,5-pentanediol can successfully proceed using Ir-Re/ $\text{SiO}_2$  (Conv. 60.3%, Select. 94.2%) [20]. On the other hand, as a conversion of HMF in water, the selectivity of 1,2,6-HT was still less than 40% as Yao and co-workers reported (Ni-Co-Al catalyst, Conv. 100 %, Select. 37.4%) [14]. For the strategy of catalyst design, both Mizugaki et al. [19] and Yao et al. [20] pointed out the importance of metal-support interface and adsorption mode of substrate for furan ring-opening reaction.

In the present study, we focus on hydrogenation of HMF with direct cleavage of furan ring to 1,2,6-HT using supported Pt catalysts. Taking the importance of adsorption state of substrate into account, the effects of various supports and the addition of cobalt oxide are investigated. Since the adsorption state of substrate was not experimentally investigated, IR spectra of adsorbed alcohol on metal oxide supports are measured. As a model molecule of HMF or BHF, methanol adsorption was conducted. The roles of metal-support interface and metal-CoO<sub>x</sub> interface are discussed.

## 2. Experimental

**2.1. Catalyst preparation.** 5 wt% Pt/MO<sub>x</sub> catalysts (MO<sub>x</sub> = CeO<sub>2</sub>, hydrotalcite, MgO, La<sub>2</sub>O<sub>3</sub>, Nd<sub>2</sub>O<sub>3</sub>, Dy<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, Ta<sub>2</sub>O<sub>5</sub>, Nb<sub>2</sub>O<sub>5</sub>, and SiO<sub>2</sub>) were prepared by an impregnation method. A aqueous suspension containing Pt(NO<sub>3</sub>)<sub>2</sub> (Pt: 0.05 g), MO<sub>x</sub> (0.95 g), and water (100 mL) was stirred for 1 h at room temperature. After evaporation in a rotary evaporator at 60 °C, the obtained cake was dried at 80 °C overnight, and calcined in air at 500 °C for 3 h. PtCo/MO<sub>x</sub> catalysts were prepared by impregnation of an aqueous solution of Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O to Pt/MO<sub>x</sub>, followed by evaporation at 60 °C, dryness at 80 °C overnight, and calcination in air at 500 °C for 3 h. The molar ratio of Pt:Co was varied from 1:9 to 9:1, and the content of Pt + Co was 5wt%.

Pt(NO<sub>3</sub>)<sub>2</sub> aqueous solution was obtained from Cataler Co. Ltd. The metal oxides for supports were obtained as follows: CeO<sub>2</sub> from Solvay, hydrotalcite from Kyowa Chemical Industry Co., Ltd., MgO from Ube Industries, Ltd., and Nb<sub>2</sub>O<sub>5</sub>·*n*H<sub>2</sub>O from CBMM. La<sub>2</sub>O<sub>3</sub>, Nd<sub>2</sub>O<sub>3</sub>, Dy<sub>2</sub>O<sub>3</sub> and Ta<sub>2</sub>O<sub>5</sub> were

purchased from Shin-Etsu Chemical Co., Ltd.  $\text{SiO}_2$  (JRC-SIO-5),  $\text{ZrO}_2$  (JRC-ZRO-5), and  $\text{Al}_2\text{O}_3$  (JRC-ALO-8) were supplied from Catalysis Society of Japan.  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (> 98 %) was purchased from Kishida Chemical Co., Ltd.

$\text{Pt}_5\text{Co}_5/\text{CeO}_2$  by colloid method was prepared as follows [21]. 0.5 mmol of  $\text{Pt}(\text{acac})_2$  (acac = acetylacetonate), 0.5 mmol of  $\text{Co}(\text{acac})_2$ , 20 mL of oleylamine were mixed at room temperature. Then the solution was further heated to 300 °C at a heating rate of 5 °C/min, the temperature was kept at 300 °C for 1 h, cooled down to room temperature. A black product was precipitated by adding 40 mL of ethanol, and separated by centrifugation. The product was dispersed in hexane, and then supported on  $\text{CeO}_2$  by impregnating the solution to  $\text{CeO}_2$ . After evaporation in a rotary evaporator, the obtained cake was dried at 80 °C overnight, and calcined in air at 700 °C for 2 min.

**2.2. Catalytic tests.** HMF was purchased from Tokyo Chemical Industry Co., Ltd. The other chemicals were purchased from Kishida Chemical Co., Ltd. Before the catalytic tests, the catalysts were reduced in  $\text{H}_2$  at 200 °C for 1 h. A 10 mg of pretreated  $\text{Pt}/\text{MO}_x$ , 0.2 mmol of HMF and 3 mL of distilled water were put into an autoclave (30 mL, Taiatsu Techno Co., TVS-1 type). The gas phase in the autoclave was replaced with ca. 1 MPa of  $\text{H}_2$  for 5 times, and finally 3 MPa of  $\text{H}_2$  was introduced. The conversion of HMF was carried out at 135 °C for 24 h. The reaction solution was analyzed using a gas chromatograph (GC, SHIMADZU GC-14A) with FID. The products were also identified using GC-MS (SHIMADZU GC-17A with GC-MS QP-5000) and  $^1\text{H}$ -NMR (Bruker 500 Ultra Shield.).

**2.3. Characterizations.** Fourier transform Infrared (FT-IR) spectra of the metal oxide supports were obtained on a JASCO FT/IR-6100 (JASCO Co.) equipped with a MCT detector at 4  $\text{cm}^{-1}$  of spectral resolution of. Metal oxides (30–200 mg) were pressed into wafers with 20 mm diameter. The wafer was pretreated under 10%  $\text{H}_2/\text{Ar}$  flow (100  $\text{mL min}^{-1}$ ) at 200 °C for 30 min, and background spectrum was recorded at 100 °C. Then, the wafer was exposed to methanol vapor (2  $\mu\text{L}$ ) under Ar flow (90  $\text{mL min}^{-1}$ ) at 100 °C. After purging by Ar at 100 °C for 3 min, FT-IR spectra of adsorbed methanol on metal oxides were recorded. Scanning transmission electron microscopy (STEM) and energy dispersive X-ray spectrometry (EDS) mapping were conducted on a JEM-2100F (JEOL) instrument operated at 200 kV.  $\text{H}_2$ -temperature programmed reduction ( $\text{H}_2$ -TPR) profiles were recorded using Microtrac-Bel BELCAT-B. A 50 mg catalyst was exposed in a flow of 5%  $\text{H}_2/\text{Ar}$  at 40  $\text{mL min}^{-1}$  and temperature raised from 50 to 500 °C at a rate of 5 °C  $\text{min}^{-1}$ . The outlet flow was analyzed by a TCD detector.

### 3. Results and Discussion

#### 3.1. Effect of supports on product selectivity.

Table 1 shows the product yields in HMF conversion using Pt catalysts supported on various metal oxides. These catalysts were classified into two groups. When hydrotalcite, MgO, and  $\text{CeO}_2$  were used as supports, 1,2,6-HT and BHTHF were preferentially produced. On the other supports, the main products were ring rearrangement products (HCPN, HCPO). Small amount of 1-hydroxyhexane-2,5-dione (HDD) was obtained on  $\text{Pt}/\text{Ta}_2\text{O}_5$ ,  $\text{Pt}/\text{Nb}_2\text{O}_5$ , and  $\text{Pt}/\text{SiO}_2$ , and 4-hydroxymethyl-2-

cyclopentenone (HCPEN) was detected on Pt/Ta<sub>2</sub>O<sub>5</sub>. The other products are not detected in GC, and considered to be polymerized products such as humic materials. It should be noted that, in addition to supported Pt catalysts, CeO<sub>2</sub> supported Ir, Ru, Pd, Ni, and Co catalysts were also examined, but the production of 1,2,6-HT was only observed on Pt/CeO<sub>2</sub>.

**Table 1** Product yields in HMF conversion using supported Pt catalysts.

Catalyst	1,2,6-HT (%)	BHTHF (%)	HCPN+HCPO (%)	HHD (%)	others (%)
Pt/hydrotalcite	32	36	1	0	31
Pt/MgO	14	34	2	0	50
Pt/CeO <sub>2</sub>	27	63	2	0	8
Pt/La <sub>2</sub> O <sub>3</sub>	0	0	84	0	16
Pt/Nd <sub>2</sub> O <sub>3</sub>	0	3	80	0	17
Pt/Dy <sub>2</sub> O <sub>3</sub>	0	0	85	0	15
Pt/Al <sub>2</sub> O <sub>3</sub>	0	0	70	0	30
Pt/ZrO <sub>2</sub>	0	0	48	0	52
Pt/Ta <sub>2</sub> O <sub>5</sub>	0	0	19	16	65
Pt/Nb <sub>2</sub> O <sub>5</sub>	0	0	24	10	66
Pt/SiO <sub>2</sub>	0	0	31	11	58

Reaction conditions: HMF 0.2 mmol, H<sub>2</sub>O 3 mL, catalyst 10mg, H<sub>2</sub> pressure 3MPa, 135 °C, 24 h. 1,2,6-HT = 1,2,6-hexanetriol, BHTHF = 2,5-bis(hydroxymethyl)-tetrahydrofuran, HCPN = 3-hydroxymethylcyclopentanone, HCPO = 3-hydroxymethylcyclopentanol, HHD = 1-hydroxyhexane-2,5-dione. Others include 4-hydroxymethyl-2-cyclopentenone (HCPEN, 18% detected only on Pt/Ta<sub>2</sub>O<sub>5</sub>) and undetectable products such as humic materials.

**Table 2** Product yields in HMF conversion using physical mixtures of Pt/SiO<sub>2</sub> and metal oxides.

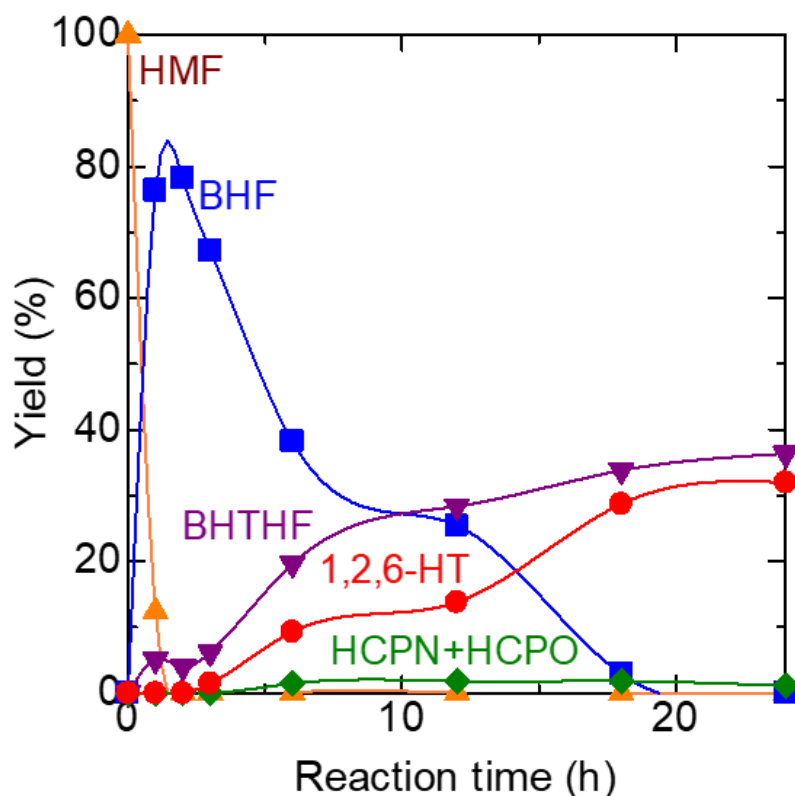
Catalyst	1,2,6-HT (%)	BHTHF (%)	HCPN+HCPO (%)	BHF (%)	others (%)
Pt/SiO <sub>2</sub> +hydrotalcite	0	4	37	19	40
Pt/SiO <sub>2</sub> +MgO	6	19	11	5	59
Pt/SiO <sub>2</sub> +CeO <sub>2</sub>	0	0	94	0	6

Reaction conditions: HMF 0.2 mmol, H<sub>2</sub>O 3 mL, catalyst 10mg, H<sub>2</sub> pressure 3MPa, 135 °C, 24 h. Weight ratio of 5wt%Pt/SiO<sub>2</sub>: metal oxide = 10 mg: 10 mg. BHF = 2,5-bis(hydroxymethyl)furan.

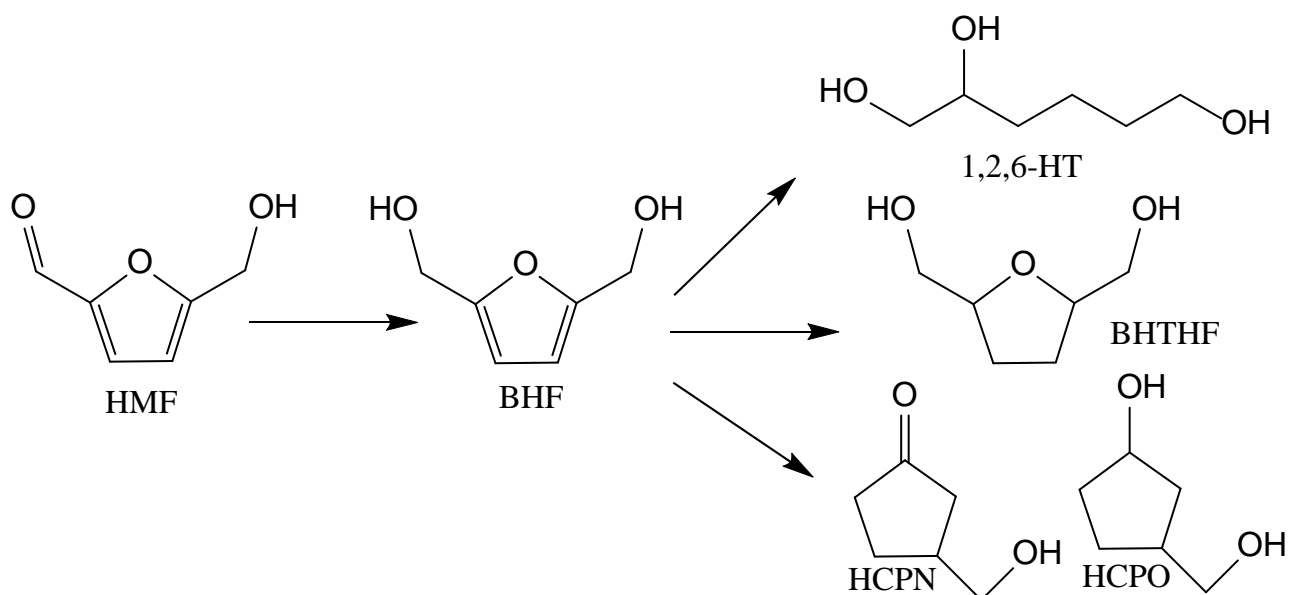
The effect of Pt-support interface was examined by comparing physical mixture of Pt/SiO<sub>2</sub> and pure supports (Table 2). SiO<sub>2</sub> was used as a chemically inert support. Comparing with Pt supported catalysts (Table 1), the products distributions are entirely different. Even when pure hydrotalcite,

MgO and CeO<sub>2</sub> were physically mixed with Pt/SiO<sub>2</sub>, 1,2,6-HT was not produced (hydrotalcite and CeO<sub>2</sub>) or was far smaller than the supported catalyst (MgO). The essential role of metal-support interface on 1,2,6-HT formation was demonstrated.

The reaction network was then investigated using Pt/hydrotalcite as a model catalyst. Figure 1 shows the dependence product distribution on reaction time for HMF conversion using Pt/hydrotalcite. At first, substrate HMF steeply decreased, and BHF yield increased. BHF yield then decreased after 2 h, instead, the yield of other products monotonously increased and further decrease was not observed. The result indicates that BHF is an intermediate, and parallel reactions proceed from BHF to other products, i.e., BHTHF, 1,2,6-HT, and cyclopentanone derivatives (HCPN, HCPO). In the separate experiment, consecutive reaction of BHTHF to 1,2,6-HT was examined. HMF was converted to BHF using Ni/SiO<sub>2</sub> at 100 °C, for 2 h in ethanol (Yield >99%). After isolation of BHTHF by evaporation at 45 °C, the obtained BHTHF was dissolved in water. Using 10 mg of Pt/hydrotalcite, the conversion of BHTHF was conducted under the same conditions (135 °C, 3MPa H<sub>2</sub>, 24 h). BHTHF did not convert to any products. No consecutive conversion of BHTHF to 1,2,6-HT was confirmed under the present reaction conditions. The reaction network can be summarized in Scheme 1: HMF is hydrogenated to BHF, then various major products, 1,2,6-HT, BHTHF, HCPN, and HCPO are parallelly produced from BHF as an intermediate. Therefore, the selective conversion of BHF is the important key for the product selectivity.



**Figure 1.** Effect of reaction time on yield of substrate and products on Pt/hydrotalcite.



**Scheme 1** Reaction network of HMF hydrogenation on Pt/hydrotalcite.

### 3.2. Structure-Activity correlation on Pt/MOx for 1,2,6-hexanetriol production.

In order to investigate the higher selectivity for 1,2,6-HT on hydrotalcite, MgO, and CeO<sub>2</sub> supported catalysts, correlations between 1,2,6-HT selectivity and various chemical properties of the supports are examined. Table 3 shows indicators of acid-base characters of metal oxide supports. IR band position of ring vibration mode of  $\nu(8a)$  of adsorbed pyridine is a good indicator of the strength of Lewis acidity, which shifts to higher wavenumber with the increase in Lewis acid strength [22]. The IR band position of C-H stretching mode of adsorbed chloroform shifts to lower wavenumber with the increase in basicity [22]. The selectivity of 1,2,6-HT can be roughly correlated to basicity of metal oxide supports, however, there are several exceptions. For examples, pH of the aqueous solution of CeO<sub>2</sub> was acidic, and Lewis acid strength and base strength of hydrotalcite were medium among the supports examined. In order to estimate pH of the aqueous solution after the conversion of HMF, we also measured pH of the aqueous solution including Pt/MOx catalysts after reduction in H<sub>2</sub> at 135 °C for 1 h. MgO, hydrotalcite, and CeO<sub>2</sub> showed the highest pH, suggesting basic property is favorable for the production of 1,2,6-HT. However, the difference in pH between CeO<sub>2</sub> and ZrO<sub>2</sub> is too small to explain the selectivity of 1,2,6-HT of these catalysts. The 1,2,6-HT selectivity cannot be rationalized only by these acid-base properties of the supports. Contribution of another factor should be considered.

For the selective diols and triol production, the importance of adsorption mode of substrate has been discussed. Mizugaki et al. reported the selective conversion of furfural to 1,2-pentanediol using Pt/hydrotalcite with a yield of 73% in 2-propanol [19]. In their report, the reaction mechanism is proposed as follows; C=O bond is at first hydrogenated to form furfuryl alcohol followed by adsorption of alkoxide species on support nearby Pt particle, and ring-opening reaction proceeds with dissociation of C-O bond in furan ring on Pt. Alkoxide species on the support is proposed to play an

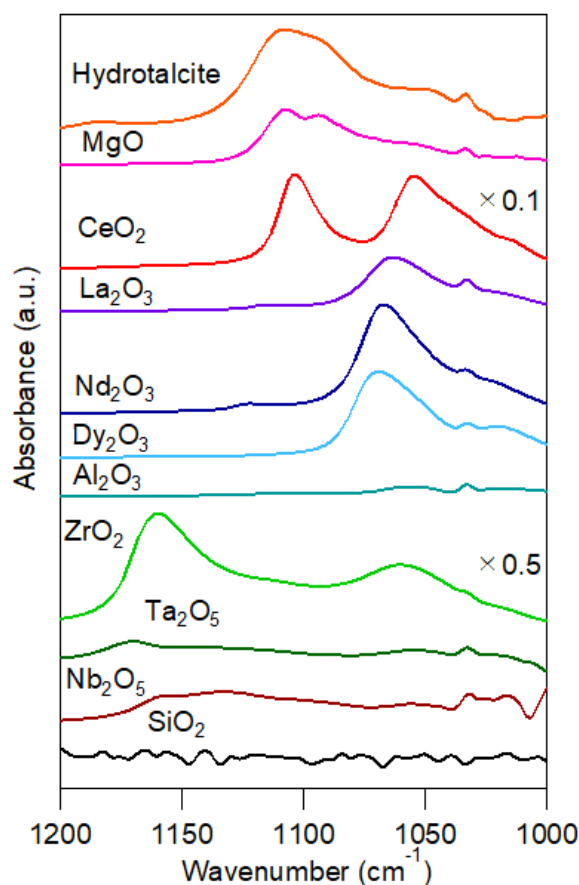
important role of ring-opening. The important role of alkoxide on metal-support interface is also proposed in other reports [23-25]. However, this proposal is not experimentally supported. Therefore, the state of adsorbed alcohol was investigated in the present study. Due to very high boiling point (275 °C) and low vapor pressure of BHF, we applied methanol as the simplest model of alcohol for IR measurement.

**Table 3** Acid-base character of metal oxide supports estimated by pH of the aqueous solution before the reaction, pH of the aqueous solution with pre-reduced (in H<sub>2</sub> at 135 °C for 1 h) Pt/MOx, IR band positions of ring vibration mode of  $\nu(8a)$  of pyridine and C-H stretching mode of chloroform.

MOx	pH with MOx	MOx	pH with reduced Pt/MOx	MOx	$\nu(8a)$ of pyridine / cm <sup>-1</sup>	MOx	$\nu(C-H)$ of chloroform / cm <sup>-1</sup>
MgO	10.7	MgO	10.3	MgO	1588	La <sub>2</sub> O <sub>3</sub>	2962
hydrotalcite	9.8	hydrotalcite	9.9	La <sub>2</sub> O <sub>3</sub>	1594	Ta <sub>2</sub> O <sub>5</sub>	2964
La <sub>2</sub> O <sub>3</sub>	7.0	CeO <sub>2</sub>	8.7	Nd <sub>2</sub> O <sub>3</sub>	1597	Nd <sub>2</sub> O <sub>3</sub>	2965
Nd <sub>2</sub> O <sub>3</sub>	6.7	ZrO <sub>2</sub>	8.5	CeO <sub>2</sub>	1598	CeO <sub>2</sub>	2970
Dy <sub>2</sub> O <sub>3</sub>	6.7	La <sub>2</sub> O <sub>3</sub>	8.4	Dy <sub>2</sub> O <sub>3</sub>	1602	Al <sub>2</sub> O <sub>3</sub>	2972
CeO <sub>2</sub>	5.7	Nb <sub>2</sub> O <sub>5</sub>	8.3	hydrotalcite	1602	MgO	2974
Al <sub>2</sub> O <sub>3</sub>	5.3	Nd <sub>2</sub> O <sub>3</sub>	8.2	ZrO <sub>2</sub>	1603	hydrotalcite	2975
ZrO <sub>2</sub>	4.9	Al <sub>2</sub> O <sub>3</sub>	7.9	Nb <sub>2</sub> O <sub>5</sub>	1604	Dy <sub>2</sub> O <sub>3</sub>	2980
Ta <sub>2</sub> O <sub>5</sub>	4.4	SiO <sub>2</sub>	7.5	Ta <sub>2</sub> O <sub>5</sub>	1607	ZrO <sub>2</sub>	3004
SiO <sub>2</sub>	4.4	Dy <sub>2</sub> O <sub>3</sub>	7.5	Al <sub>2</sub> O <sub>3</sub>	1614	Nb <sub>2</sub> O <sub>5</sub>	3020
Nb <sub>2</sub> O <sub>5</sub>	4.3	Ta <sub>2</sub> O <sub>5</sub>	7.3	SiO <sub>2</sub>	N.D.	SiO <sub>2</sub>	N.D.

Figure 2 shows IR spectra of adsorbed methanol on pure supports at 100 °C after purging gas phase methanol in a flow of Ar for 3 min. The spectra shows three types of  $\nu(O-C)$  vibration bands: The bands around 1160 cm<sup>-1</sup> for ZrO<sub>2</sub>, Nb<sub>2</sub>O<sub>5</sub>, and SiO<sub>2</sub>, the bands around 1100 cm<sup>-1</sup> for hydrotalcite, MgO, and CeO<sub>2</sub>, and the bands below 1060 cm<sup>-1</sup> for CeO<sub>2</sub>, La<sub>2</sub>O<sub>3</sub>, Nd<sub>2</sub>O<sub>3</sub>, Dy<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, and ZrO<sub>2</sub>. The bands around 1160 cm<sup>-1</sup> and 1100 cm<sup>-1</sup> are assigned to monodentate surface methoxide, and the bands below 1060 cm<sup>-1</sup> are assigned to bidentate surface methoxide, respectively [26–31]. The broadening of the band below 1060 cm<sup>-1</sup> to lower wavenumber suggests the presence of other species: bidentate species with different coordination (1045 cm<sup>-1</sup>) and triply coordinated methoxy species (1012 cm<sup>-1</sup>). Interestingly, the monodentate methoxide band at 1100 cm<sup>-1</sup> was observed only on hydrotalcite, MgO, and CeO<sub>2</sub>, on which 1,2,6-HT and BHTHF were selectively produced. The selective production of 1,2,6-HT can be correlated to the monodentate adsorption mode on the supports. However, another monodentate species around 1160 cm<sup>-1</sup> was observed on ZrO<sub>2</sub>, Nb<sub>2</sub>O<sub>5</sub>,

and  $\text{SiO}_2$ , on which 1,2,6-HT was not produced. It should be noted only these catalysts produced 1-hydroxyhexane-2,5-dione (HDD) which suggests direct ring-opening of HMF (Table 1). Without monodentate adsorption on  $\text{La}_2\text{O}_3$ ,  $\text{Nd}_2\text{O}_3$ ,  $\text{Dy}_2\text{O}_3$ , and  $\text{Al}_2\text{O}_3$ , the ring rearrangement reaction to form cyclopentanone derivatives (HCPN+HCPO) preferentially proceeded. The monodentate alkoxide adsorption is essential for ring-opening reaction, however, another factor is necessary for 1,2,6-HT production. The acid-base properties of the supports (Table 2) indicates that Pt/MOx on basic supports (hydrotalcite, MgO, and  $\text{CeO}_2$ ) produced 1,2,6-HT, while Pt/MOx on acidic or inert supports ( $\text{Ta}_2\text{O}_5$ ,  $\text{Nb}_2\text{O}_5$ ,  $\text{SiO}_2$ ) produced HDD. These results indicate the importance of both basic property of supports and monodentate adsorption of BHF on Pt-support interface for the selective production of 1,2,6-HT. Hydrotalcite, MgO, and  $\text{CeO}_2$  gave preferential metal-support interface to from monodentate alkoxide on basic supports, however, the yield of 1,2,6-HT is still lower than 40%. Then we examined the addition of  $\text{CoO}_x$  as a promoter.



**Figure 2.**  $\nu(\text{O-C})$  vibration region of IR spectra of adsorbed methanol on various metal oxide supports.

### 3.3. Addition of $\text{CoO}_x$ as a promoter

Although the strong effect of supports on the product selectivity was observed in the previous section, the yield of 1,2,6-HT was still lower than 40%. Then, as another strategy to promote hexanetriol selectivity, we examined the addition of  $\text{CoO}_x$  which is reported to be effective for the



hydrogen ring-opening reaction in organic solvents [25, 32-24]. Table 4 shows the effect of the supports on the product distributions using PtCo/MO<sub>x</sub> for HMF conversion in water. When loading amount was Pt:Co =5:5, CeO<sub>2</sub>, hydrotalcite, MgO showed high selectivity to hexanetriol, and 1,2,6-HT yield exceeded 40% only when CeO<sub>2</sub> was used as the support (42%). Comparing PtCo/CeO<sub>2</sub>, and Pt/CeO<sub>2</sub>, the addition of CoO<sub>x</sub> improved the selectivity of 1,2,6-HT by the sacrifice of BHTHF selectivity, which means that CoO<sub>x</sub> enhanced the C-O cleavage of furan ring by suppressing hydrogenation of furan ring [14]. Table 3 also shows the effect of Pt:Co ratio. The best selectivity for 1,2,6-HT was observed on Pt:Co = 5:5.

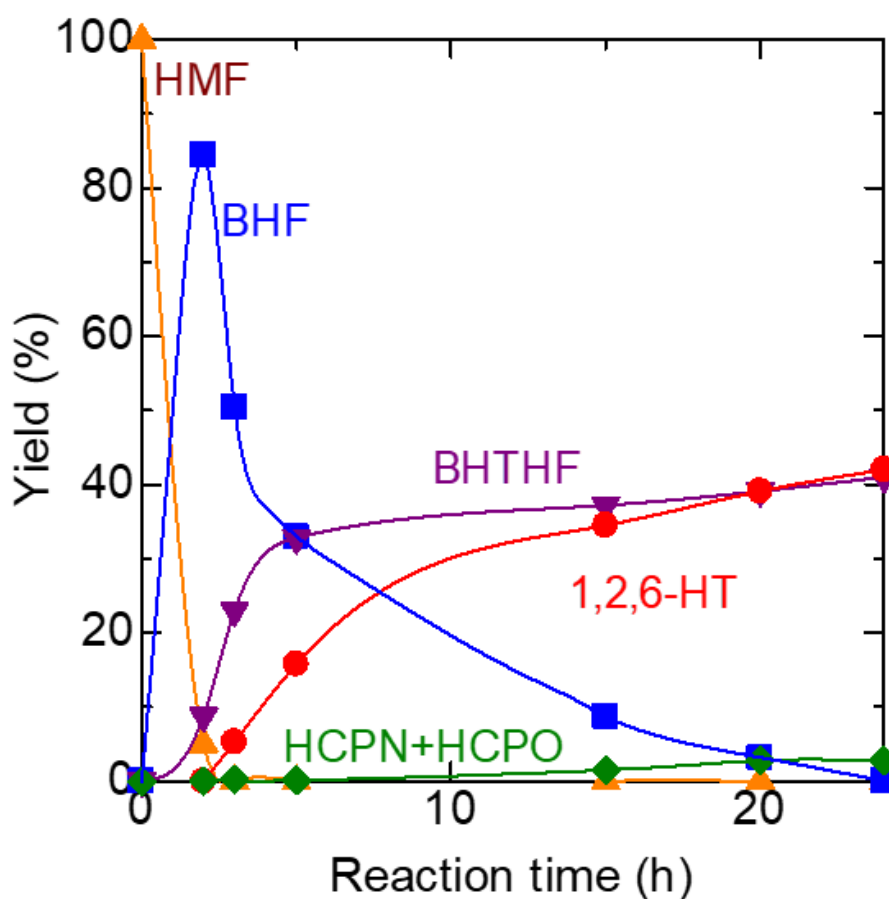
The effect of the contact between Pt and Co was also examined. Alloying of Pt and Co was examined using Pt<sub>5</sub>Co<sub>5</sub>/CeO<sub>2</sub> catalyst prepared by colloid method as reported by Yu et al. [21]. The total yield of 1,2,6-HT and BHTHF was less than 10%, while cyclohexanone derivatives (HCPN+HCPO) were the main products. The alloying of Pt-Co is not effective for the target reaction, and Pt and CoO<sub>x</sub> should be exist as individual particles. However, a physical mixture of Pt/CeO<sub>2</sub> and Co<sub>3</sub>O<sub>4</sub> showed almost the same yield to Pt/CeO<sub>2</sub>. Pt/Co<sub>3</sub>O<sub>4</sub> showed low selectivity to 1,2,6-HT. These results suggest that the added CoO<sub>x</sub> should be exist as small particles, nearby Pt particle on CeO<sub>2</sub>, controlling parallel reaction from BHF to 1,2,6-HT or BHTHF.

**Table 4** Product yields in HMF conversion using Co-promoted supported Pt catalysts.

Catalyst	1,2,6-HT (%)	BHTHF (%)	HCPN+HCPO (%)	others (%)
Pt <sub>5</sub> Co <sub>5</sub> /CeO <sub>2</sub>	42	41	7	10
Pt <sub>5</sub> Co <sub>5</sub> /hydrotalcite	31	42	0	27
Pt <sub>5</sub> Co <sub>5</sub> /MgO	23	52	0	25
Pt <sub>5</sub> Co <sub>5</sub> /SiO <sub>2</sub>	0	0	91	9
Pt <sub>5</sub> Co <sub>5</sub> /Al <sub>2</sub> O <sub>3</sub>	11	15	28	46
Pt/CeO <sub>2</sub>	27	63	2	8
Pt <sub>9</sub> Co <sub>1</sub> /CeO <sub>2</sub>	30	54	1	15
Pt <sub>7</sub> Co <sub>3</sub> /CeO <sub>2</sub>	33	48	2	17
Pt <sub>5</sub> Co <sub>5</sub> /CeO <sub>2</sub>	42	41	7	10
Pt <sub>3</sub> Co <sub>7</sub> /CeO <sub>2</sub>	30	42	11	17
Pt <sub>1</sub> Co <sub>9</sub> /CeO <sub>2</sub>	32	42	6	20
Co/CeO <sub>2</sub>	0	0	0	35
Pt/Co <sub>3</sub> O <sub>4</sub>	3	13	17	67
Physical mixture of Pt/CeO <sub>2</sub> + Co <sub>3</sub> O <sub>4</sub>	26	34	8	32
Pt <sub>5</sub> Co <sub>5</sub> /CeO <sub>2</sub> (colloid method)	2	8	61	29

Reaction conditions: HMF 0.2 mmol, H<sub>2</sub>O 3 mL, catalyst 10mg, H<sub>2</sub> pressure 3MPa, 135 °C, 24 h. For the physical mixture, a mixture of 10 mg Pt/CeO<sub>2</sub> and 10 mg Co<sub>3</sub>O<sub>4</sub> is used.

The dependence product distribution on reaction time for reductive conversion of HMF on Pt<sub>5</sub>Co<sub>5</sub>/CeO<sub>2</sub> is shown Figure 3. The trends in the product distribution were almost the same to Pt/hydrotalcite, i.e., the substrate HMF at first steeply decreased, BHF yield showed the maximum at 3 h, and then the yield of 1,2,6-HT and BHTHF monotonously increased without further decrease. The cyclopentanone derivatives (HCPN, HCPO) were negligible. Although the reaction scheme was almost the same, the higher selectivity of 1,2,6-HT with the sacrifice of BHTHF was obtained. The reaction was stopped completely by the removal of Pt<sub>5</sub>Co<sub>5</sub>/CeO<sub>2</sub> from the reaction solution. After the reaction mixture had been stirred for 3 h (HMF conversion at 100 % and yields of BHF, BHTHF, and 1,2,6-HT are 50%, 23%, 5.3%, respectively), the catalyst was removed by filtration. The reaction did not proceed with the obtained solution by heating under 1 MPa H<sub>2</sub> at 135 °C for 24 h. The result excludes a possible contribution of homogeneous catalysis by leached species.



**Figure 3.** Effect of reaction time on yield of substrate and products on Pt/hydrotalcite.

The product selectivity was strongly affected by the reduction temperature of Pt<sub>5</sub>Co<sub>5</sub>/CeO<sub>2</sub>, as

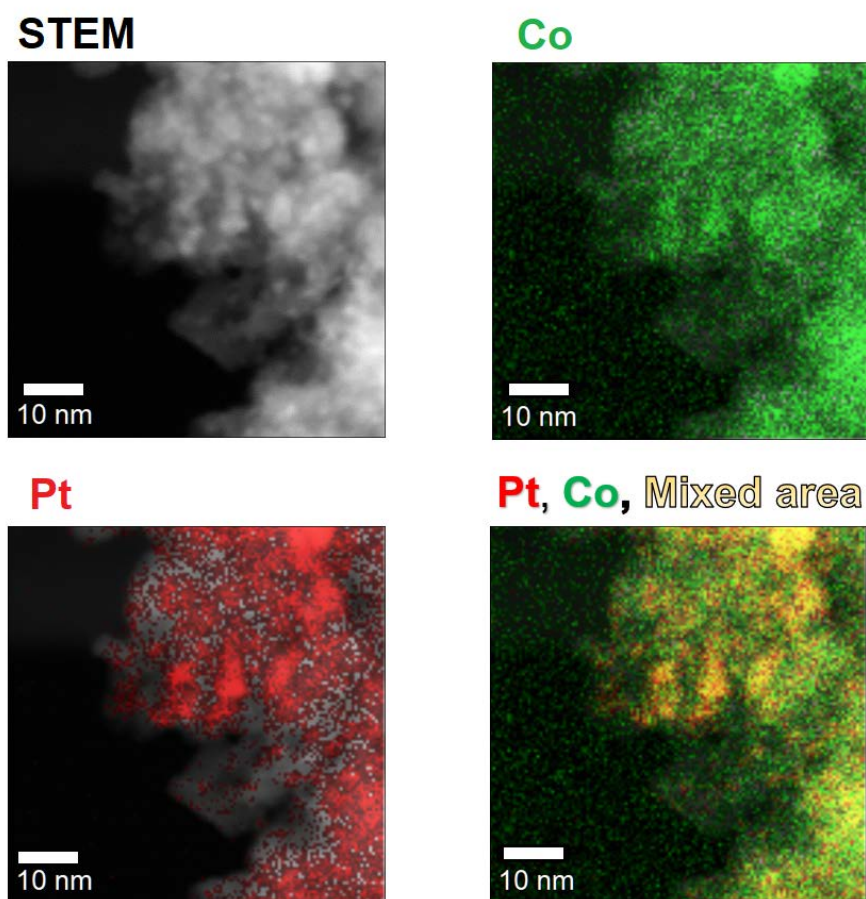
shown in Table 5. Without pre-reduction in H<sub>2</sub>, the hexanetriol yield was below 40%. The maximum yield of 1,2,6-HT was obtained when the catalyst was reduced in H<sub>2</sub> at 200 °C (42%), while further increase in the reduction temperature decreased the hexanetriol yield.

**Table 5** Effect of pre-reduction temperature of Pt<sub>5</sub>Co<sub>5</sub>/CeO<sub>2</sub> on product yields in HMF conversion.

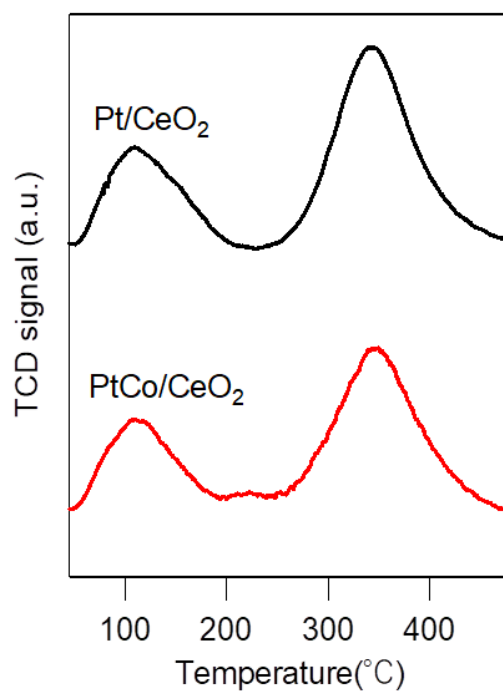
Pre-reduction	1,2,6-HT (%)	BHTHF (%)	HCPN+HCPO (%)	others (%)
As prepared	37	43	3	17
Reduced in H <sub>2</sub> at 200 °C	42	41	7	10
Reduced in H <sub>2</sub> at 300 °C	30	45	3	22
Reduced in H <sub>2</sub> at 400 °C	33	44	4	19
Reduced in H <sub>2</sub> at 500 °C	30	47	4	19

Reaction conditions: HMF 0.2 mmol, H<sub>2</sub>O 3 mL, catalyst 10mg, H<sub>2</sub> pressure 3MPa, 135 °C, 24 h.

The structure of Pt<sub>5</sub>Co<sub>5</sub>/CeO<sub>2</sub> was characterized. Figure 4 shows STEM-EDX images of Pt<sub>5</sub>Co<sub>5</sub>/CeO<sub>2</sub>. In the elemental mapping, red, green, and yellow dots show the presence of Pt, Co, and the mixed region, respectively. The positions of red dots agree well with those of green dots, indicating Pt and Co were well mixed, in other words, Co-species are positioned nearby Pt particles. The particle size of Pt was around 3-5 nm from STEM. The formation of Pt-Co alloy can be rejected because Pt<sub>5</sub>Co<sub>5</sub>/CeO<sub>2</sub> prepared by the colloid method showed very low selectivity to 1,2,6-HT (Table 5). The Co-species exists as small particles nearby Pt particles. In order to examine the effect of pre-reduction temperature, H<sub>2</sub>-TPR was conducted and the profiles are shown in Figure 5. The profile of Pt/CeO<sub>2</sub> showed two reduction peaks, assignable to Pt oxide reduction to Pt<sup>0</sup> at 80–170 °C and the reduction of CeO<sub>2</sub> surface at 300–400 °C [35]. In the profile of Pt<sub>5</sub>Co<sub>5</sub>/CeO<sub>2</sub>, an additional small reduction peak was also observed at 200–260 °C. Luo et al. reported detailed assignment of H<sub>2</sub>-TPR profile of PdCo/CeO<sub>2</sub> [36]. H<sub>2</sub>-TPR of supported CoO<sub>x</sub> gives two step reduction profiles: The first reduction of Co<sub>3</sub>O<sub>4</sub> to CoO at 154 °C, and the second reduction of CoO to metallic Co at 368 °C [36]. The lower reduction temperature than metal-free CoO<sub>x</sub>/CeO<sub>2</sub> is due to hydrogen spillover [37]. According to their report, the reduction peak above 200 °C is assigned to the second reduction of CoO to metallic Co, i.e., the H<sub>2</sub> pre-treatment at 200 °C results in the first reduction of Co<sub>3</sub>O<sub>4</sub> to CoO, and the highest yield of 1,2,6-HT was obtained when the state of supported cobalt is CoO.



**Figure 4.** STEM-EDX images of  $\text{Pt}_5\text{Co}_5/\text{CeO}_2$ .



**Figure 5.** Profiles of  $\text{H}_2$ -temperature programmed reduction of  $\text{Pt}/\text{CeO}_2$  and  $\text{Pt}_5\text{Co}_5/\text{CeO}_2$ .

It is reported that  $\text{CoO}_x$  provides adsorption sites for C=C bond [38], which promotes C-O bond cleavage of furan ring [14, 39]. Yao et al. correlated the promoted ring-opening reaction over Ni-Co-Al mixed oxide to tilted adsorption of BHF by the effect of CoO [14]. The adsorption mode of BHF determine the selectivity to 1,2,6-HT or BHTHF: Tilted adsorption of BHF proceed ring opening reaction by C-O cleavage to form 1,2,6-HT, while parallel adsorption of BHF proceeds hydrogenation of furan ring to form BHTHF. The promotion of ring-opening reaction over  $\text{Pt}_5\text{Co}_5/\text{CeO}_2$  can be rationalized as follows: BHF is adsorbed on  $\text{CeO}_2$  by forming surface methoxide, leading adsorption of C=C bond of BHF on CoO nearby Pt particle by forming tilted BHF adsorption, which results in the selective C-O bond cleavage to form 1,2,6-HT.

## Conclusion

The effects of supports and  $\text{CoO}_x$  addition on one-pot conversion of 5-hydroxymethylfurfural to 1,2,6-hexanetriol in water solvent were investigated using supported Pt catalysts. By using Pt catalysts supported on hydroctalcite, MgO, and  $\text{CeO}_2$ , 1,2,6-hexanetriol was obtained. The essential role of metal-support interface, i.e., monodentate alkoxide adsorption and basic property of supports, are clarified. Further improvement of 1,2,6-hexanetriol yield was achieved by the addition of cobalt oxide. The maximum yield of 1,2,6-hexanetriol (42%) was obtained using  $\text{Pt}_5\text{Co}_5/\text{CeO}_2$  catalyst pre-reduced at 200 °C. The interface of Pt particles and CoO particles on  $\text{CeO}_2$  was suggested to be important for the selective 1,2,6-hexanetriol formation.

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