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Supplementary Information

Dihydroxyacetone Production by Glycerol Oxidation under Moderate Condition Using Pt Loaded on La_{1-x}Bi_xOF Solids

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Experimental

La_{1-x}Bi_xOF was prepared using a conventional solid-state reaction. La₂O₃ (99.99%, Shin-Etsu Chemical Co., Ltd.), LaF₃ (99.9%, Kojundo Chemical Laboratory Co., Ltd.), and Bi₂O₃ (99.9%, KISHIDA CHEMICAL Co., Ltd.) were mixed in a La:Bi:O:F molar ratio of (1-x):x:1:1 and grounded using an agate mortar and a pestle. The mixture was calcined at 600 °C for 12 h under the air flow. SBA-16 was prepared via a hydrothermal method according to literatures.^{1,2} To a grinding bowl (agate) equipped with grinding balls (agate) were added La_{1-x}Bi_xOF (76.2 mg), SBA-16 (400.0 mg), and ethanol (5 mL). Ball milling was performed with a Fritsch Pulverisette 7 planetary micro mill (300 rpm, 3 h). After removal of ethanol, the solid was heated at 500 °C for 4 h under air to give 16 wt% La_{1-x}Bi_xOF/SBA-16. Pt loading was performed by the impregnation method; 16 wt% La_{1-x}Bi_xOF/SBA-16 was impregnated in an aqueous colloidal solution of Pt nanoparticles stabilized by poly(*N*-vinyl-2pyrrolidone) (TANAKA Kikinzoku Kogyo K.K.), where the Pt amount was adjusted to 7 wt%. After removal of water, the solid was calcined at 500 °C for 4 h under air to give 7 wt% Pt/16 wt% La_{1-x}Bi_xOF/SBA-16. For the comparison purpose, 7 wt% Pt/16 wt% La_{0.95}Bi_{0.05}O_{1.5}/SBA-16 was prepared without using LaF₃.

X-ray fluorescence (Supermini200, Rigaku Corporation) analysis was conducted to determine the composition of the catalysts. X-ray powder diffraction (XRD; SmartLab, Rigaku Corporation) measurements were performed with Cu Kα radiation (40 kV, 30 mA), and the Pt crystallite size was estimated using the Scherrer equation. The nitrogen adsorption–desorption measurements were carried out at approximately –196 °C to assess the BET specific surface area (TriStar 3000, Shimadzu Corporation). X-ray photoelectron spectroscopy (XPS; PHI5000 VersaProbe II, ULVAC-PHI, Inc.) was performed at room temperature using Al Kα radiation. Here, the effect of charging on the binding energies was corrected with respect to the C 1s peak at 284.6 eV, and the spectra were fitted using a Shirley background and Gaussian–Lorentzian line shapes.

Pt L₃-edge X-ray absorption spectroscopy (XAS) experiments were performed at BL-12C of KEK using Si(111) double-crystal monochromatized synchrotron radiation under the ring-conditions of 2.5 GeV and 450 mA. All experiments were performed using the transmission mode with a quick scan technique (QXAFS) at room temperature. The ionization chambers were used to measure the intensities of the incident (I_0) and transmitted (I) X-rays. XAS analysis was conducted using Demeter package, a comprehensive system for processing and analyzing X-ray absorption spectroscopy data.^{3–5} Background removal and normalization of raw data were performed using Athena software. E_0 was defined as photon energy at the absorption edge where μ T = 0.5 in the normalized $\mu(E)$ spectrum. The E_0 value of the Pt foil was set to 11564 eV for photon energy calibration. The extracted k^2 -weighted extended X-ray absorption fine structure (EXAFS) oscillation ($k^2\chi(k)$) was Fourier transformed in the *k*-range of 3–13 Å⁻¹, and the thus-generated FT($k^2\chi(k)$) data was fitted in *r*-space in the *r*-range of 1.3–3.3 Å using Artemis software. Single scattering paths were calculated using FEFF 6 code built in this package. The intrinsic loss factor of S_0^2 = 1.34 was obtained from the fitting of Pt foil. One fitting parameter was used for the absorption edge energy correction (ΔE_0) for the Pt–Pt and Pt–O shells to reduce the number of fitting parameters. Other EXAFS parameters,

including the coordination number (CN), bond length (R), and Debye–Waller factor (σ^2) were variable. Wavelet transformation (WT)⁶ of k^2 -weighted EXAFS was performed using Morlet wavelet function with the scaling parameters of $\sigma = 1$ and $\kappa = 6$ (k-range: 3–14 Å⁻¹, r-range: 0.5–5 Å). The samples for the measurement and appropriate amount of boron nitride were ground using an agate mortar for 30 min under an ambient atmosphere. The resulting powder was pelletized using a tablet press ($\phi = 10$ mm, JASCO Corporation) and hydraulic press (CMD-5PA, RIKEN KIKI Co., Ltd.) at pressures ranging from 10 to 15 MPa. The prepared pellet was packed in a gas-barrier bag (thickness: 60 µm) and subjected to XAS measurements.

Transmission electron microscopy (TEM) images were recorded using a JEOL JEM-2100 electron microscope at an accelerating voltage of 200 kV using a Holey carbon support film-coated Cu microgrid (U1003, EMJapan Co., Ltd.). Temperature programmed reduction (H₂-TPR) measurements were carried out using a MicroTracBEL BELCAT catalyst analyzer under a flow of 5 vol% H₂-95 vol% Ar (50 mL·min⁻¹) at a heating rate of 5 °C·min⁻¹ up to 500 °C.

The liquid-phase oxidation of glycerol was conducted in a flask equipped with a condenser (4 °C) in an open-air system, and 10 mL of 1.0 wt% glycerol aq. was mixed with 0.3 g of the prepared catalyst in a flask; subsequently, it was stirred at 30 °C without applying pressure or oxygen gas bubbling. The liquid phase (0.01 mL) was analyzed using a high-performance liquid chromatography (HPLC, JASCO Corporation) system equipped with a refractive index (RI) and photodiode array (PDA) detector, where the product was separated using Shodex Sugar SH-1011 (Showa Denko Ceramics Co., Ltd.) column operating at 50 °C with H₂SO₄ aq. (5 mmol·L⁻¹) as the eluent flowing at 0.75 mL·min⁻¹. The glycerol conversion, product yield, and product selectivity were estimated according to the following equations:

(Glycerol conversion) = 1 - [Glycerol] / [Glycerol]₀ (Product yield) = [Product] / [Glycerol]₀ (product selectivity) = (product yield) / (glycerol conversion),

where $[glycerol]_0$ and [glycerol] represent the glycerol concentrations (mol·L⁻¹) before and after the reaction, respectively. [Product] represents the concentration (mol·L⁻¹) of the product after the reaction. Each concentration was determined using the external calibration curve method. After the reaction for 4 h, the mixture was centrifuged to separate the catalyst and the liquid-phase (Allegra 64R Centrifuge, Beckman Coulter). The crystal phase of the used catalyst was analyzed by the XRD measurement (SmartLab, Rigaku Corporation) and the metal leaching was assessed using XRF (EDX-720, Shimadzu Corporation). To investigate the effect of the promoter, a catalytic activity test was carried out under N₂ gas bubbling at 30 °C. Similarly, catalytic activities for glyceraldehyde (1.0 wt%) and dihydroxyacetone (1.0 wt%) were examined.



Figure S1. XRD pattern of the $La_{1-x}Bi_xOF$ sample.



Figure S2. XRD pattern of the LaOF/SBA sample.

Sample	Pt crystallite size / nm	Specific surface area / m ² ·g ⁻¹
Pt/LaOF/SBA	6.1	425
Pt/La _{0.97} Bi _{0.03} OF/SBA	6.5	403
Pt/La _{0.95} Bi _{0.05} OF/SBA	6.3	435
Pt/La _{0.93} Bi _{0.07} OF/SBA	6.5	377

Table S1. Pt crystallite size and specific surface area of Pt/La_{1-x}Bi_xOF/SBA



Figure S3. Nitrogen adsorption–desorption isotherms of Pt/La_{0.95}Bi_{0.05}OF/SBA, La_{0.95}Bi_{0.05}OF/SBA, and SBA-16. The isotherm curve for SBA-16 showed type-IV hysteresis loop, assigned as the mesoporous material according to IUPAC classification. Similar isotherm curves were obtained for La_{0.95}Bi_{0.05}OF/SBA and Pt/La_{0.95}Bi_{0.05}OF/SBA, indicating that the mesoporous structure was preserved after the La_{0.95}Bi_{0.05}OF/SBA and Pt loading.



Figure S4. TEM images of Pt/La_{0.95}Bi_{0.05}OF/SBA. The regular arrangement of mesopores (approximately 13 nm) was observed. Pt nanoparticles were observed as dark spots with approximately 6 nm diameters.

Table S2. Measured compo	DSITION OF PT/La _{1-x} BI _x OF/SBA
Feed composition	Measured composition
7.0wt%Pt/16wt%LaOF/SBA-16	7.6wt%Pt/13wt%LaOF/SBA-16
7.0wt%Pt/16wt%La _{0.97} Bi _{0.03} OF/SBA-16	8.1wt%Pt/14wt%La _{0.98} Bi _{0.02} OF/SBA-16

 $7.0wt\%Pt/16wt\%La_{0.95}Bi_{0.05}OF/SBA-16$

able S2. Measured	composition	of Pt/La ₁₋	_x Bi _x OF/SBA
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 $7.5wt\%Pt/17wt\%La_{0.96}Bi_{0.04}OF/SBA-16$



Figure S5. XPS spectra of Pt 4f core level for $Pt/L_{a0.95}Bi_{0.05}OF/SBA$ and Pt/LaOF/SBA. The binding energies of Pt $4f_{7/2}$ and Pt $4f_{5/2}$ can be identified as divalent Pt^{2+} (76 and 73 eV) and Pt^{0} (74 and 71 eV). The $Pt^{2+}/(Pt^{2+}+Pt^{0})$ ratios of $Pt/La_{0.95}Bi_{0.05}OF/SBA$ and Pt/LaOF/SBA were estimated to be 17.9% and 14.3%, respectively.



Figure S6. Pt L₃-edge XAS data of Pt/La_{0.95}Bi_{0.05}OF/SBA: a) XANES spectra; b) k^2 -weighted FT-EXAFS; c) k^2 -weighted EXAFS oscillations; d) k^2 -weighted WT-EXAFS. MS denotes multiple scattering. e) Plots of the fitted curve in *r*-space: magnitude and its imaginary part.



Figure S7. Pt L₃-edge XAS data of Pt/LaOF/SBA, Pt/La_{0.97}Bi_{0.03}OF/SBA, and Pt/La_{0.95}Bi_{0.05}OF/SBA.

	shell	CN^a	$\Delta E_0 (eV)^b$	σ² (10 ⁻³ Å) ^c	R (Å) ^d	χν ^{2e}	<i>R</i> -factor (%) ^f	
	Pt–Pt	6.4 ± 0.8	9.8 ± 1.2	7.6 ± 0.8	2.759 ± 0.006	- 212.02	1 0	
Pt/LaOF/SBA	Pt–O	1.5 ± 0.5	9.8 ± 1.2	9.4 ± 0.5	1.984 ± 0.017	- 313.03	1.3	
Pt/La _{0.97} Bi _{0.03} OF/SB	Pt–Pt	6.7 ± 0.7	9.5 ± 1.1	7.8 ± 0.7	2.758 ± 0.006	- 224 51	1 1	
A	Pt–O	1.4 ± 0.5	9.5 ± 1.1 9.4 ± 0.5 1.980		1.980 ± 0.017	- 234.51	1.1	
Pt/La _{0.95} Bi _{0.05} OF/SB	Pt–Pt	6.2 ± 0.8	10.5 ± 1.3	6.9 ± 1.0	2.764 ± 0.007	294.65	1.6	
А	Pt–O	1.5 ± 0.6	10.5 ± 1.3	10.4 ± 6.4	2.023 ± 0.021		1.0	

Table S3. Parameters obtained from the fitting analysis of $FT(k^2\chi(k))$ data

k-range: 3–13 Å⁻¹. *r*-range: 1.3–3.3 Å. ^{*a*}Coordination number. ^{*b*}Absorption edge energy correction. ^{*c*}Debye–Waller factor. ^{*d*}Atomic distance. ^{*e*}Reduced χ-squared value. ^{*f*}Goodness-of-Fit index.

The X-ray absorption near edge structure (XANES) of Pt/La_{0.95}Bi_{0.05}OF/SBA was similar to that of the Pt foil rather than PtO₂, while the peak intensity at the white line (11569 eV) was higher than that of the Pt foil (Fig. S6a). This result suggested the formation of high-valent Pt species along with Pt⁰ nanoparticles, which is consistent with the XPS results. In addition, k^2 -weighted Fourier transform of the extended X-ray absorption fine structure (FT-EXAFS) of Pt/La_{0.95}Bi_{0.05}OF/SBA showed that the intensity of the peak at 1.7 Å corresponding to the Pt–O scattering increased slightly compared with that of Pt foil, which also suggests the formation of high-valent Pt species (Fig. S6b). For further confirmation, the wavelet analysis was conducted. The k^2 -weighted EXAFS oscillations were wavelet-transformed to generate WT-EXAFS and visualize as a 2D contour map (Fig. S6d). In the case of Pt foil, the strongest WT-EXAFS signal was observed in the (k,R) = (8,3) region which corresponds to the Pt–Pt scattering, while other regions were weaker than this. Meanwhile, the magnitude of WT-EXAFS of Pt/La_{0.95}Bi_{0.05}OF/SBA at the (k,R) = (5,2) region was comparable that of (k,R) = (8,3). These results evidently indicated that the FT-EXAFS at 1.7 Å contains the Pt–O scattering. Hence, the fitting of the FT-EXAFS was performed with two shells, Pt–O and Pt– Pt, and found that the coordination numbers (CN) of oxygen and platinum at the nearest neighbour are 1.5 and 6.2, respectively (Fig. S6e and Table S3). Given the small CN_{Pt-Pt} value and the absence of the scattering from platinum atoms at the second coordination sphere, the thus-prepared platinum nanoparticles consist of amorphous platinum oxide and Pt⁰ nanoparticles, rather than the surface-oxidized Pt nanoparticles. This model is good agreement with the absence of diffraction signals corresponding to the crystalline platinum oxides, such as PtO and PtO₂, in XRD. Fitting analysis was also performed for Pt/LaOF/SBA and Pt/La_{0.97}Bi_{0.03}OF/SBA (Fig. S7 and Table S3), however, few substantial differences in catalyst composition were found.



Figure S8. XRD patterns of fresh and used Pt/La_{0.95}Bi_{0.05}OF/SBA. No crystal structural change was observed.



Figure S9. XRD patterns of $La_{0.95}Bi_{0.05}O_{1.5}$ and 7 wt% Pt/16 wt% $La_{0.95}Bi_{0.05}O_{1.5}$ /SBA-16, which do not contain the F element. The $La_{0.95}Bi_{0.05}O_{1.5}$ sample had a single-phase of the hexagonal La_2O_3 structure. In the case of 7 wt% Pt/16 wt% $La_{0.95}Bi_{0.05}O_{1.5}$ /SBA-16, the XRD pattern displayed the peaks of Pt and the broad peak derived from SBA-16, where no peaks related to the La_2O_3 phase could be observed.

Table S4. Glycerol conversion and product yields for the $Pt/La_{0.95}Bi_{0.05}O_{1.5}/SBA$ catalyst (1 wt% glycerol 10 mL, 0.3 g of catalyst, the atmospheric open-air, 30 °C, 4 h)

Chicaral conversion / %	Yield / %							
	DHA	HA	GLA	GA	ТА	MA	GLOA	OA
4.2	2.1	0	1.4	1.4	0	0	0	0

Table S5. Glycerol conversion and product yields for the Pt/La_{0.95}Bi_{0.05}OF/SBA catalyst under nitrogen gas bubbling (1 wt% glycerol 10 mL, 0.3 g of catalyst, nitrogen gas bubbling, 30 °C, 4 h)

Glycerol conversion / %	Yield / %							
	DHA	HA	GLA	GA	ТА	MA	GLOA	OA
6.3	3.7	0	1.8	0	0	0	0	0

Table S6. Glycerol conversion and product yields for the $La_{0.95}Bi_{0.05}OF/SBA$ sample without Pt (1 wt% glycerol 10 mL, 0.3 g of catalyst, the atmospheric open-air, 30 °C, 4 h)

Glycerol conversion / %	Yield / %							
	DHA	HA	GLA	GA	ТА	MA	GLOA	OA
3.4	2.7	0	0	0	0	0	0	0

Table S7. Catalytic activities for GLA oxidation over $Pt/La_{0.95}Bi_{0.05}OF/SBA$ and Pt/LaOF/SBA catalysts (1 wt% GLA 10 mL, 0.3 g of catalyst, the atmospheric open-air, 30 °C, 4 h)

Catalyst G	CLA Conversion / %		Yield / %						
	GLA COnversion / %	DHA	HA	GA	ТА	MA	GLOA	OA	
Pt/LaOF/SBA	52.0	0	1.1	42.3	0.2	0	9.0	0	
Pt/La _{0.95} Bi _{0.05} OF/SBA	74.4	0	52.0	22.5	0.4	0.8	10.8	3.0	

Table S8. GLA conversion and product yields for the Pt/La_{0.95}Bi_{0.05}OF/SBA catalyst under nitrogen gas bubbling (1 wt% GLA 10 mL, 0.3 g of catalyst, nitrogen gas bubbling, 30 °C, 4 h)

GLA conversion / %		Yield / %						
GLA COnversion / %	DHA	HA	GA	ТА	MA	GLOA	OA	
11.4	0	2.8	5.9	0	0	1.4	0.2	

Catalyst DHA (DHA Conversion / %				Yield / %)		
	DHA CONVERSION / 76	HA	GLA	GA	ТА	MA	GLOA	OA
Pt/LaOF/SBA	31.0	24.4	0	0	0	0	2.1	0
Pt/La _{0.95} Bi _{0.05} OF/SBA	22.9	11.0	0	0	0	0	4.8	0

Table S9. Catalytic activities for DHA oxidation over $Pt/La_{0.95}Bi_{0.05}OF/SBA$ and Pt/LaOF/SBA catalysts (1 wt% DHA 10 mL, 0.3 g of catalyst, the atmospheric open-air, 30 °C, 4 h)

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