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Electronic Supplementary Information

Hydrodeoxygenation of phenols as lignin models under acid-free conditions with carbon-supported platinum catalysts

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1. Experimental

1.1. Chemicals

Activated carbons were purchased from Aldrich [activated charcoal Norit SX Ultra, denoted as AC(N)] and Wako [activated charcoal, denoted as AC(W)]. CMK-3 was prepared according to a literature (S. Jun, S. H. Joo, R. Ryoo, M. Kruk, M. Jaroniec, Z. Liu, T. Ohsuna, O. Terasaki, *J. Am. Chem. Soc.*, 2000, **122**, 10712). Multi-walled carbon nanotube was purchased from TCI [20−40 nm (diameter) and 1−2 μm (length) from TCI; 30−70 nm (diameter) by TEM analysis, denoted as MWCNT]. Carbon black was supplied by Cabot (Black pearls 2000, denoted as BP2000). Zirconia (JRC-ZRO-2), alumina (JRC-ALO-2), and ceria (JRC-CEO-2) were supplied by Catalysis Society of Japan. Titania (P-25) was supplied by Aerosil Japan. $H_2PtCl_6·6H_2O$, $PdCl_2$, and $RhCl_3·3H_2O$ were purchased from Kanto Chemicals. $RuCl_3·xH_2O$ was purchased from Wako Pure Chemical. 4-Propylphenol, 4-propylcyclohexanol, and 4-allylguaiacol (eugenol) were purchased from TCI. 4-Propylguaiacol (dihydroeugenol), and 4-allyl-2,6-dimethoxyphenol were purchased from Wako Pure Chemicals. 4-Acetonylguaiacol (4-hydroxy-3-methoxyphenylacetone) was purchased from Aldrich.

1.2. Preparation of catalysts

1.2.1. Carbon-supported catalysts

Carbon-supported metal catalysts were prepared by a conventional impregnation method. Typically, an aqueous solution of H_2PtCl_6 (0.209 mmol in 5 mL water; Pt metal loading 2 wt%) was added to a mixture of AC(N) (2.00 g) and water (35 mL). The reaction mixture was stirred at RT for 24 h, evaporated to dryness, and dried under vacuum. The sample was reduced in a fixed-bed flow reactor with H_2 (30 mL min^{-1}) at 400 °C for 2 h to give Pt/AC(N) catalyst.

1.2.2. Oxide-supported catalysts

Oxide-supported Pt catalysts were prepared by a conventional impregnation method. Typically, an aqueous solution of H_2PtCl_6 (0.209 mmol in 5 mL water; Pt metal loading 2 wt%) was added to a mixture of ZrO_2 (2.00 g) and water (35 mL). The reaction mixture was stirred at RT for 24 h, evaporated to dryness, and dried under vacuum. The sample was calcined in a fixed-bed flow reactor with O_2 (30 mL min^{-1}) at 400 °C for 2 h, then reduced with H_2 (30 mL min^{-1}) at 400 °C for 2 h to give Pt/ZrO_2 catalyst.

1.3. Characterization

N_2 adsorption-desorption analyses were carried out at −196 °C with BEL Japan BELSORP-mini II. Specific surface areas of sample were calculated according to the Brunauer–Emmett–Teller (BET) method. Pore size distributions were estimated by the Barrett–Joyner–Halenda (BJH) and micropore (MP) methods. Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku MiniFlex using Cu Kα radiation (λ = 0.15418 nm) at 30 kV and 15 mV. Transmission electron microscopy (TEM) was performed with a JEOL JEM-2000ES at an accelerating voltage of 200 kV. Ammonia temperature-programmed desorption (NH_3-TPD) was measured with a BEL Japan BELCAT-A equipped with a thermal conductivity detector (TCD) and a mass spectrometer (MS) for continuous analysis of the desorbed species. The sample (0.05 g) was placed in a quartz tube and purged with He, then heated with a temerature ramp of 3 °C/min to 400 °C under H_2 flow. After 2 h at 400 °C, the sample was cooled down to 100 °C under He flow. Ammonia saturation was carried out at 100 °C using a 5% NH_3-He gas mixture for 0.5 h. Then, excess ammonia was removed by purging with He for 0.5 h. The desorption step was carried out with a temperature ramp of 10 °C/min from 100 to 600 °C under He flow. The amount of desorbed ammonia was measured with a MS detector ($m/z = 16$).

1.4. Catalytic hydrodeoxygenation of phenols in water

A typical procedure: 4-propylphenol (10 mmol, 1.36 g), 2 wt% Pt/AC(N) (98 mg, S/C = 1000), and water (40 mL) were charged in a well dried high-pressure reactor (OM Lab-Tech MMJ-100, SUS316, 100 mL). The autoclave was heated at 280 °C for 2 h with stirring at 600 rpm after pressurization with H_2 to 4 MPa at RT. After cooling to RT, the reaction mixture was extracted with ethyl acetate and the organic layer was analyzed by GC and GC-MS using 2-isopropylphenol as an internal standard. The aqueous layer was also analyzed by GC using *N*,*N*-dimethylformamide (DMF) as an internal standard. GC analyses were carried out using a Shimadzu GC-14B equipped with an integrator (C-R8A) with a capillary column (HR-1, 0.25 mm i.d. ×50 m). GC-MS analyses were measured by a Shimadzu GC-2010/PARVUM2 equipped with a capillary column (HR-1, 0.25 mm i.d. × 50 m). The pH of the aqueous solution after the reaction was checked with a Horiba pH meter D-51. The catalyst was recovered by centrifugation, followed by washing with ethyl acetate and water, and drying in an oven at 120 °C for 2 h. Then, the catalyst was reused for the next reaction.

1.5. Catalytic hydrodeoxygenation of 4-propylphenol under solvent-free conditions

4-Propylphenol (10 mmol, 1.36 g) and 2 wt% Pt/AC(N) (98 mg, S/C = 1000) were charged in a well dried high-pressure reactor (OM Lab-Tech MMJ-100, SUS316, 100 mL). The autoclave was heated at 280 °C for 4 h with stirring at 600 rpm after pressurization with H_2 to 4 MPa at RT. After cooling to RT, the reaction mixture was extracted with ethyl acetate and the solution was analyzed by GC and GC-MS using 2-isopropylphenol as an internal standard. The catalyst was recovered by centrifugation, followed by washing with ethyl acetate, and drying in an oven at 120 °C for 2 h. Then, the catalyst was reused in the next reaction.

2. Results

Characterization of carbon-supported Pt catalysts.

Carbon-supported Pt catalysts were characterized by N_2 adsorption, XRD, and TEM analyses. The structural parameters were summarized in Table S1. Pt catalysts supported on AC(N), AC(W), CMK-3, and BP2000 have high BET surface areas of ca. 1000 $m^2 g^{-1}$ with micro- and mesopores. On the other hand, Pt/MWCNT has much lower surface area (94 $m^2 g^{-1}$) and a larger pore size. The Pt particle sizes of Pt/AC(W) and Pt/MWCNT were ca. 2 nm by applying the Scherrer's equation in XRD analyses, while the XRD patterns of the other Pt catalysts showed no peaks of Pt crystals, suggesting that the Pt nanoparticles were highly dispersed (< 2 nm) on the surface of the carbon supports (Fig. S1). TEM analyses revealed that the Pt nanoparticles of 1–2 nm were formed on the supports, which were in good agreement with the XRD data (Table S1 and Fig. S2).

Table S1 Structural parameters of carbon-supported Pt catalysts.

Catalyst [a]	S_{BET} [b] ($m^2 g^{-1}$)	V_p [c] ($cm^3 g^{-1}$)	d_p [d] (nm)	d_{XRD} [e,f] (nm)	d_{TEM} [e,g] (nm)
Pt/AC(N)	994	0.86	0.8 [h]	–	1.5 ± 0.3
Pt/AC(W)	1250	1.18	1.5 [h]	2.4	2.3 ± 0.4
Pt/CMK-3	1155	1.31	3.8 [i]	–	1.1 ± 0.2
Pt/MWCNT [j]	94	0.89	52 [i]	2.2	2.0 ± 0.6
Pt/BP2000	1543	3.08	0.8 [h]	–	1.1 ± 0.3

[a] 2 wt% Pt loading. [b] BET (Brunauer-Emmett-Teller) surface area. [c] Total pore volume at $P/P_0 = 0.99$. [d] Average pore diameter. [e] Mean diameter of Pt particle. [f] By XRD analysis. [g] By TEM analysis. [h] By MP (micropore) method. [i] By BJH (Barrett-Joyner-Halenda) method. [j] The outer diameter of MWCNT determined by TEM is 30–70 nm.

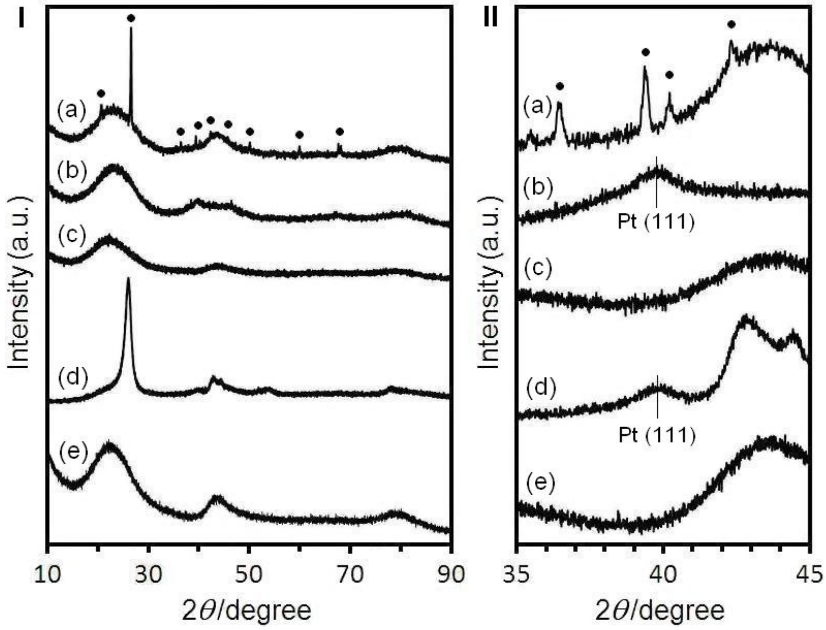


Fig. S1 XRD patterns of (a) 2 wt% Pt/AC(N), (b) 2 wt% Pt/AC(W), (c) 2 wt% Pt/CMK-3, (d) 2 wt% Pt/MWCNT, and (e) 2 wt% Pt/BP2000 at wide 2θ angles (I) and at selected 2θ angles (II). ●: Sharp peaks in the XRD pattern (a) are derived from quartz, which is an impurity of AC(N) support.

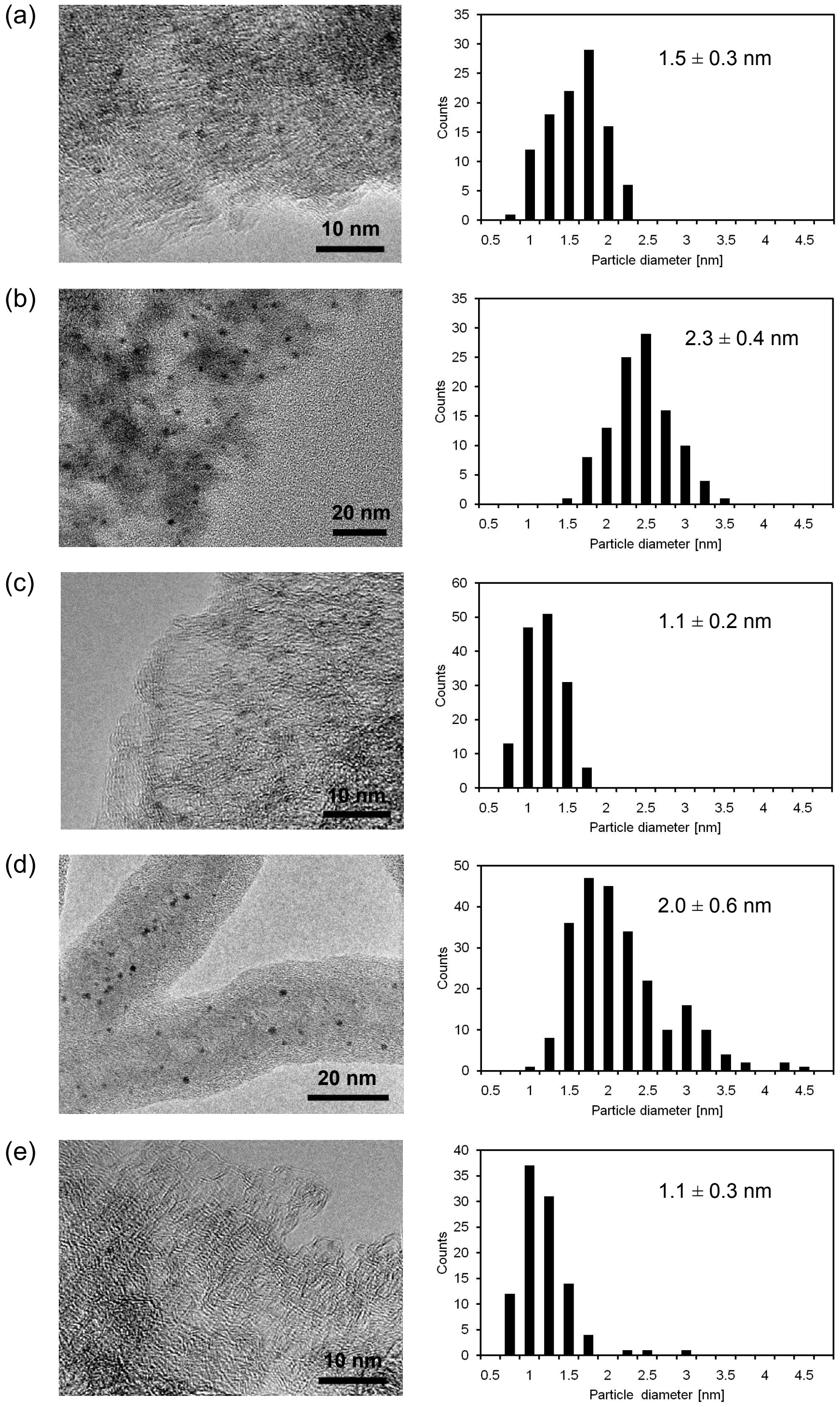


Fig. S2 TEM images and Pt particle size distributions of (a) 2 wt% Pt/AC(N), (b) 2 wt% Pt/AC(W), (c) 2 wt% Pt/CMK-3, (d) 2 wt% Pt/MWCNT, and (e) 2 wt% Pt/BP2000.

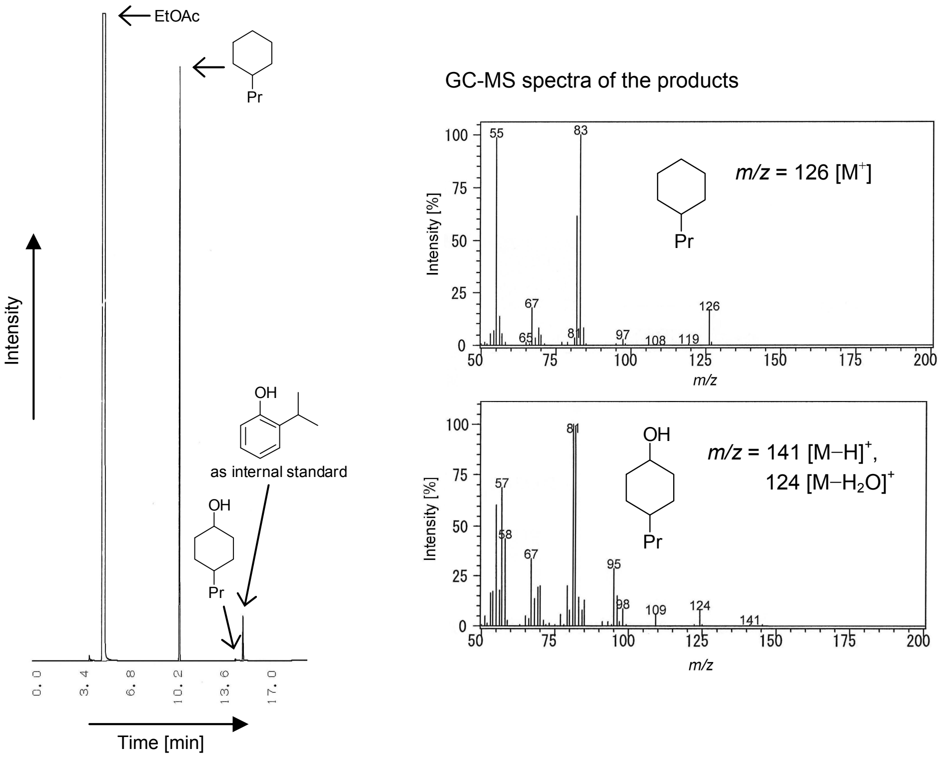


Fig. S3 Gas chromatogram of organic layer after the hydrodeoxygenation of 4-propylphenol (**1**) with Pt/AC(N) catalyst (Table 1, entry 1).

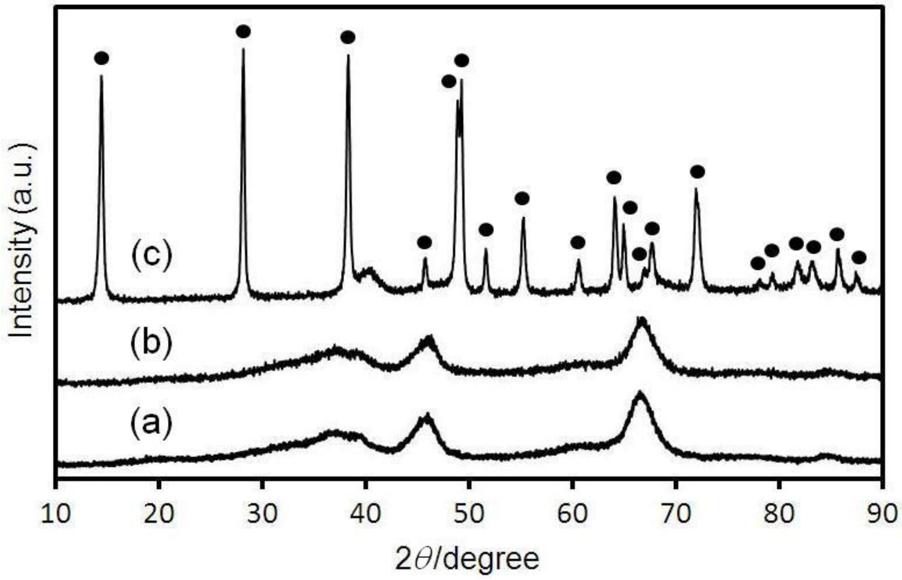


Fig. S4 XRD patterns of (a) γ-Al_2O_3, (b) 2 wt% Pt/γ-Al_2O_3 before the reaction, and (c) Pt/γ-Al_2O_3 after the reaction (Table 1, entry 9). ●: Boehmite.

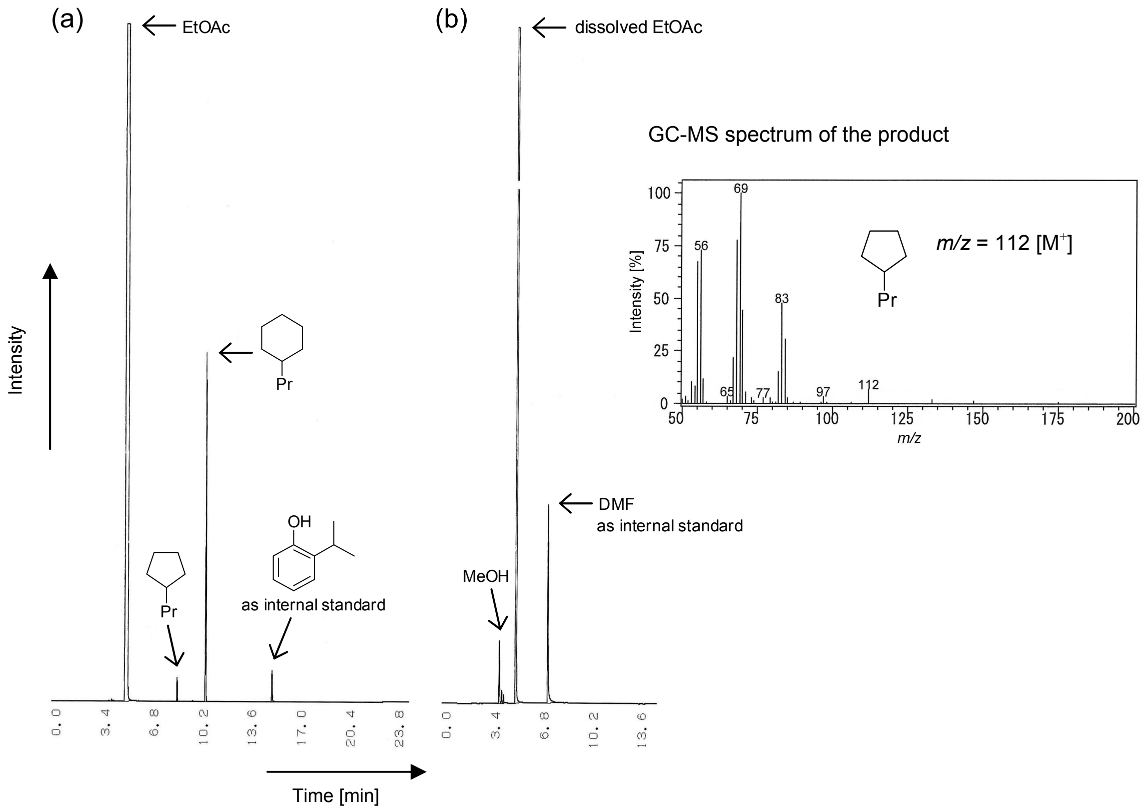
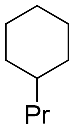
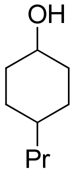
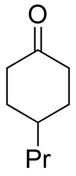
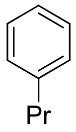


Fig. S5 Gas chromatogram of (a) organic and (b) aqueous layer after the hydrodeoxygenation of 4-propylguaiacol (**6**) with Pt/AC(N) catalyst (Table 2, entry 16).

Table S2 Reuse experiments of 2 wt% Pt/AC(N) catalyst for the hydrodeoxygenation of 4-propylphenol (**1**) in water and under solvent-free conditions.[a]

Entry	Run	Solvent	Conversion (%)	 **2**	 **3**	 **4**	 **5**
1 [b]	1st	H_2O	100	>99	0	0	0
2 [b]	2nd	H_2O	100	>99	0	0	0
3 [b]	3rd	H_2O	100	>99	0	0	0
4 [c]	1st	–	100	>99	0	0	0
5 [c]	2nd	–	100	99	1	0	0
6 [c]	3rd	–	100	99	1	0	0

[a] Reaction conditions: **1** (10 mmol, 1.36 g), 2 wt% Pt/AC(N) (1st run: 98 mg, S/C = 1000), water (40 mL) or no solvent, initial H_2 pressure at RT = 4 MPa, 280 °C, stirred at 600 rpm. [b] Reaction time: 2 h. [c] Reaction time: 4 h.

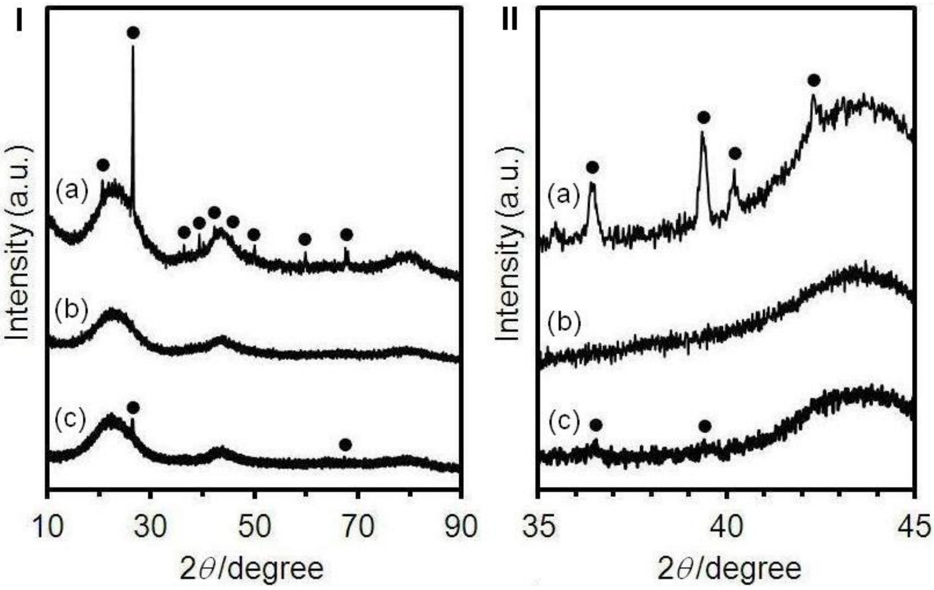


Fig. S6 XRD patterns of Pt/AC(N) before and after the reuse experiments at wide 2*θ* angles (I) and at selected 2*θ* angles (II). (a) 2 wt% Pt/AC(N) before the reaction, (b) Pt/AC(N) after the reuse experiments in water (Table S2, entry 3, 3rd run), and (c) Pt/AC(N) after the reuse experiments under solvent-free conditions (Table S2, entry 6, 3rd run). ●: Sharp peaks in the XRD patterns (a) and (c) are derived from quartz, which is an impurity of AC(N) support. As seen in the XRD pattern (b), the impurity was washed out from the Pt/AC(N) catalyst during the repeated catalytic runs.

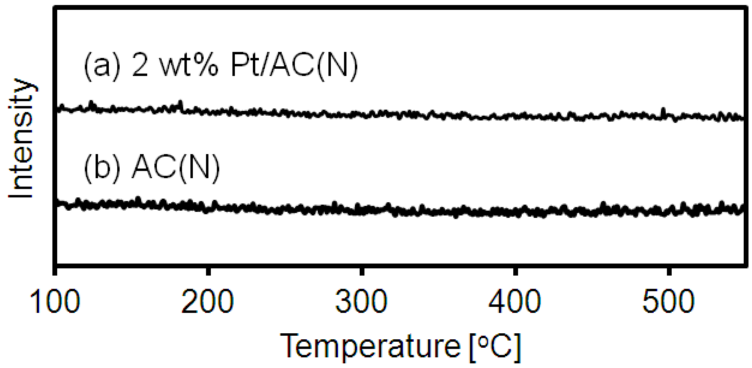


Fig. S7 Ammonia temperature-programmed desorption (NH_3-TPD) profiles of (a) 2 wt% Pt/AC(N) and (b) AC(N).