Supplementary Information (SI) for Catalysis Science & Technology.

Supplementary Information

Reductive CO_2 Fixation by *N*-Formylation Reaction over Supported Pt Nanoparticle Catalyst Modified with Basic Polyoxometalates

Soichi KIKKAWA,[a] Yutaro MATSUNAGA,[a] Shoji FUKUDA,[a] and Seiji YAMAZOE [a*]*

Chemicals

γ-Al_2O_3 (JRC-ALO-7), ZrO_2 (JRC-ZRO-6), Nb_2O_5 (JRC-NBO-2), and TiO_2 (JRC-TIO-17) were supplied from the Catalyst Society of Japan. Aqueous solution of $Pt[(NH_3)_2(NO_2)_2]$ was purchased from Furuya Metal Co. Ltd. $K_8Nb_6O_{19}\cdot 14H_2O$ and $K_8Ta_6O_{19}\cdot 16H_2O$ were purchased from Mitsuwa Chemical Co. Ltd. Methanol (MeOH), dodecane, piperidine, piperazine, methylpiperazine, morpholine, 1,2,3,4-tetrahydroisoquinoline, nitrophenol, 1-formylpiperidine, dimetylamine, and toluene were purchased from Tokyo Chemical Industry Co. Ltd. Potassium carbonate, nitric acid, and hydrogen fluoride were purchased from Kanto Chemical Co. Inc. All reagents were used as received.

Synthesis of POM-modified supported Pt NP catalyst

Supported Pt catalysts (Pt/Al_2O_3) were prepared by a typical impregnation method, in accordance with a previous report.[13] Al_2O_3 was dispersed in an aqueous solution of $Pt[(NH_3)_2(NO_2)_2]$ (equivalent to 5.0wt$_{Pt}$%) and then evaporated at 80°C. The resulting sample was calcined in air at 673 K for 5 h and then reduced in 5% H_2 (100 mL/min) at 673 K for 2 h to obtain Al_2O_3-loaded Pt NPs (Pt/Al_2O_3). $[M_6O_{19}]^{8-}$-modified Pt/Al_2O_3 (M = Nb, Ta, M6-Pt/Al_2O_3) was prepared by an adsorption method. Pt/Al_2O_3 (600 mg) was dispersed in 100 mL of 61.5 mM $K_8Nb_6O_{19}$ and $K_8Ta_6O_{19}$ aqueous solutions (POM/Pt atomic ratio = 4:1) under a N_2 atmosphere, followed by suction filtration and drying. The amount of modifying $[Nb_6O_{19}]^{8-}$ was controlled by the concentration of $K_8Nb_6O_{19}$ aq. for the absorption treatment ($[Nb_6O_{19}]^{8-}$/Pt atom = 0.006–4). The samples were referred to using the POM/Pt atomic ratio during the absorption process as ***X*M6-Pt/Al$_2$O$_3$** (M = Nb, Ta). ZrO_2, Nb_2O_5, and TiO_2 were also used as support in the same manner.

Catalytic reaction

The *N*-formylation of amines using CO_2 as a carbon source was carried out in an autoclave. Typical reaction conditions for the *N*-formylation of piperidine are as follows: piperidine, 0.1 mmol; methanol, 2 mL; catalyst, 19.5 mg (Pt; equivalent to 5.0 μmol); internal standard, dodecane; CO_2, 1.0 MPa; H_2, 2.0 MPa; reaction temperature, 130°C; and reaction time, 72 h. For the blank tests, Nb_2O_5 (1.8 mg), NH_4Cl (6.2 μmol), Cs_2CO_3 (0.31 μmol), and 0.1 mL of 3.1 mM $K_8Nb_6O_{19}$ aq. (0.31 μmol) were added as additives to **Pt/Al$_2$O$_3$**. As for P_{CO2} and P_{H2} dependence, P_{CO2} and P_{H2} were varied in the ranges of 0.1–1.0 and 0.1–2.0, respectively. To confirm the applicability of *N*-formylation reactions, piperazine, methylpiperazine, morpholine, and 1,2,3,4-tetrahydroisoquinoline were used as amines. As for the *N*-formylation of morpholine, 2 mL of DMF was used as a solvent.

The products were quantified using a gas chromatograph equipped with a flame ionization detector (GC-2014; Shimadzu Co. Ltd.). The conversion and yield were calculated as follows:

$$Conversion\ (\%) = \left(1 - \frac{Area_{Sub.}}{Area_{IS}} \times \frac{Area_{IS,0}}{Area_{Sub.,0}}\right) \times 100$$

$$Yield\ (\%) = \frac{Area_{Pro.}}{Area_{IS}} \times \frac{ECN_{Sub.}}{ECN_{Pro.}} \times \frac{Area_{IS,0}}{Area_{Sub.,0}} \times 100$$

where Sub. stands for amine substrate; IS, internal standard (dodecane); Pro., product; and ECN, effective carbon number. Subscript 0 indicates the peak area reaction solution without catalyst.

Characterization

The loading amounts of Pt NPs, and $[Nb_6O_{19}]^{8-}$ and $[Ta_6O_{19}]^{8-}$ clusters were determined by inductively coupled plasma atomic emission spectroscopy (ICP-OES, iCAP 6200; Thermo Fisher Scientific). The catalysts were dissolved in a mixed solution of HNO_3 and HF at a volume ratio of 4:1 by heating at 363 K.

The size distribution of Pt NPs was observed using a high-angle annular dark field scanning transmission electron microscope (HAADF-STEM, ARM-200F NEOARM; JEOL) operated at 200 kV. The fluorescent X-rays of Nb K- and Pt L-edges for Nb6-Pt/Al_2O_3 and Ta M- and Pt L- and M-edges for Ta6-Pt/Al_2O_3 were used for line analysis of STEM images using an energy-dispersive X-ray (EDX) analyzer.

X-ray absorption spectroscopy was carried out on the BL01B1 beamline at SPring-8 (Japan Synchrotron Radiation Research Institute). Nb K-, and Pt and Ta L_3-edges X-ray absorption fine structure (XAFS) spectra were collected using a double-crystal Si(311) or Si(111) monochromator, respectively, while rejecting the higher harmonic X-rays using a Rh-coated mirror. The incident and transmitted X-ray fluxes were measured using ionization chambers. Data reduction was performed using xTunes software.[14]

The base property of $[Nb_6O_{19}]^{8-}$-modified Pt NPs was confirmed by the coloration of *p*-nitrophenol. The catalyst powders were dispersed in a MeOH solution of *p*-nitrophenol and the filtrate was measured using a UV-vis spectrometer (V-700; JASCO). In the presence of base, the solution turned to yellow by the formation of phenoxide ions.

CO pulse titration was carried out to determine the Pt dispersion (BELCAT-II; Microtrac MRB Co. Ltd.). As a pretreatment, the catalyst was oxidized at 623 K under 100% O_2 and then reduced at 623 K under 2% H_2/Ar. The amount of Pt atoms exposed at the surface per gram of catalyst was determined using CO pulse titration at 323 K, assuming a chemisorption stoichiometry of CO:Pt = 1.

The surface electronic state of Pt NPs was evaluated by diffuse reflectance Fourier-transform infrared spectroscopy (IR-DRIFTS) using CO as a probe. The measurement was performed using an infrared spectrometer (FT/IR-4700; JASCO) equipped with a mercury cadmium tungsten detector. The spectra were collected with the integration of 128 scans with a resolution of 4 cm^{-1}. As a pretreatment, the catalyst was oxidized at 623 K under 100% O_2 and then reduced at 623 K under 2% H_2/Ar. The difference spectrum was obtained by a subtraction of sample spectra w/o CO adsorption from that under 5% CO/He.

Table S1. Comparison of the catalytic activity in this work with the reported catalytic systems

Catalyst	Metal (Loading (μmol))	Additive	Substrate (mmol)	Reaction temperature (K)	Reaction time (h)	Yield (%)	TOF (h^{-1})	Ref.
Nb6-4.0Pt/Al_2O_3	Pt (5)	None	Piperidine (0.1)	403	72	84	0.24	This work
–	–	None	Morpholine (0.1)	403	72	71	0.20	This work
K-$Pt(Nb_6O_{19})_2]^{12-}$	Pt (20)	None	Piperidine (1.0)	403	36	71	0.99	Ref. [7]
–	–	None	Morpholine (0.5)	403	48	83	0.43	Ref. [7]
$Cu(OCOCH_3)_2$	Cu (100)	4-Dimethyl aminopyridine	Morpholine (1.0)	363	12	>99	0.83	Ref. [10]
(Methyltrioctylammonium)$_6$-$SiW_{11}O_{39}Ru$	Ru (5.0)	1-Butyl-3-methyl-imidazolium acetate	Morpholine (1.0)	393	12	97	16	Ref. [14]
Co_3O_4	Co (85)	$ZnCl_2$	Isoquinoline (0.5)	443	16	97	0.36	Ref. [9]
Cu_0/CuAlOx (Cu 7.5wt%)	Cu (118)	None	Morpholine (1.0)	423	24	>99	0.35	Ref. [16]
Pd/C (Pd: 1wt%)	Pd (4.7)	KOH	Piperidine (1.0)	378	5	51	22	Ref. [17]
Au/TiO_2 (Au: 2.2wt%)	Au (10)	Dimethylamine	Morpholine (0.5)	398	5	>99	4.4	Ref. [18]
Au/Nb_2O_5 (Au: 1wt%)	Au (10)	N,N-Dimethyl acetamide	Morpholine (0.5)	398	5	69	6.9	Ref. [19]
Ir/nanodiamond @graphite (Ir: 0.03wt%)	Ir (0.049)	None	Morpholine (735)	423	23	46	3.1×10^5	Ref. [13]

Table S2. Solvent effect on *N*-formylation reaction of piperidine using CO_2 over **4.0Nb6-Pt/Al_2O_3**[a].

Entry	Solvent	Yield (%)	CO production[b] (mmol)
1	MeOH	43	91.4
2	Dimetylamine	75	29.6
3	Toluene	84	13.7

[a] Amines, 0.1 mmol; solvent, 2 mL; catalyst, 19.5 mg; internal standard, dodecane; CO_2, 1.0 MPa; H_2, 2.0 MPa; reaction temperature, 130°C; reaction time, 72 h.

[a] Produced amount of CO was calculated from the concentration of CO after the reaction, initial total pressure (3.0 MPa), and volume of reaction vessel (40 mL).

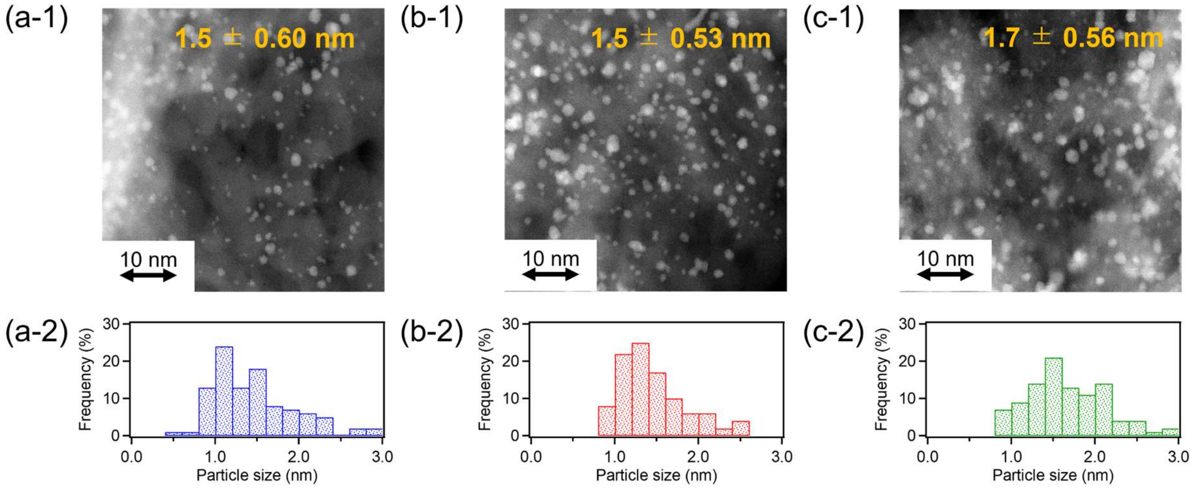

Figure S1. HAADF-STEM images of (a-1) **Pt/Al$_2$O$_3$**, (b-1) **4.0Nb6- Pt/Al$_2$O$_3$**, (c-1) **4.0Ta6-Pt/Al$_2$O$_3$**, and the corresponding particle size distributions (a-2), (b-2), and (c-2), respectively.

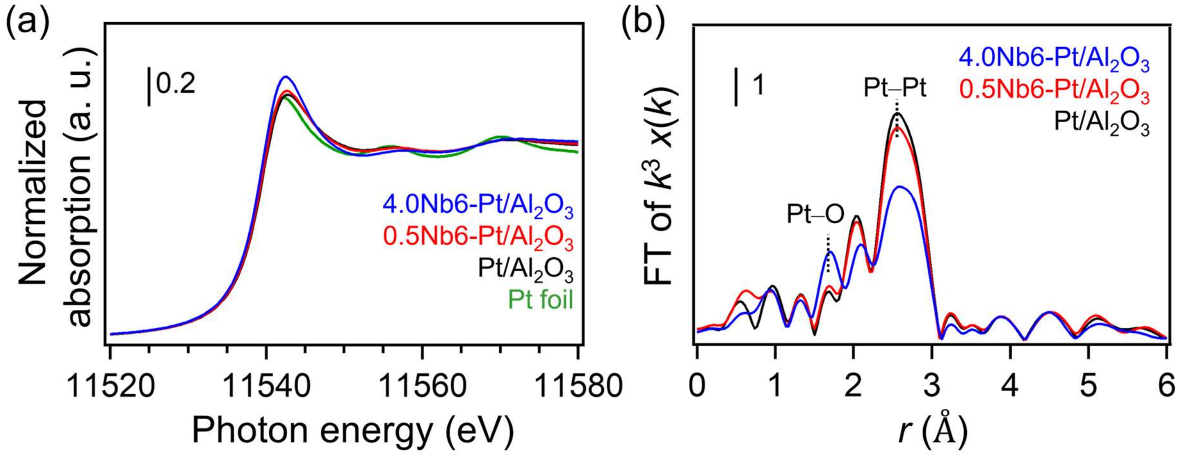

Figure S2. (a) Pt L$_3$-edge XANES spectra of **4.0Nb6-Pt/Al$_2$O$_3$** (blue), **0.5Nb6-Pt/Al$_2$O$_3$** (red), **Pt/Al$_2$O$_3$** (black), and Pt foil (green). (b) FT of Pt L$_3$-edge EXAFS spectra of **4.0Nb6-Pt/Al$_2$O$_3$** (blue), **0.5Nb6-Pt/Al$_2$O$_3$** (red), and **Pt/Al$_2$O$_3$** (black).

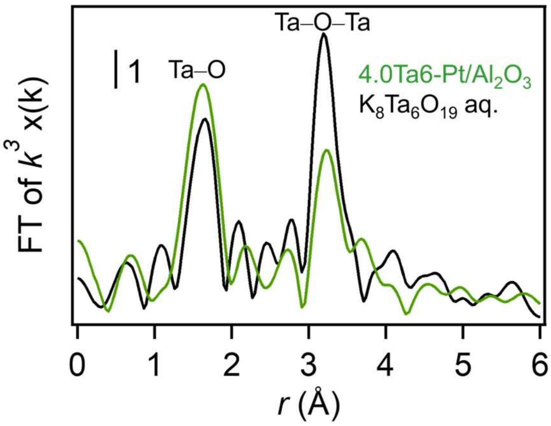

Figure S3. FT of Ta L_3-edge EXAFS spectra of **4.0Ta6-Pt/Al$_2$O$_3$** (green) and $K_8Ta_6O_{19}$ aqueous solution (black).

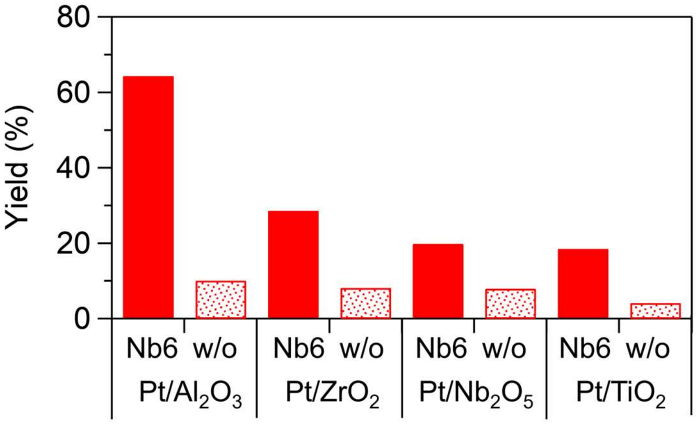

Figure S4. Product yield in *N*-formylation reaction of piperidine over supported Pt NP catalysts with various supports. The loading weight of Pt was 5wt%. The dispersions of Pt NPs measured by CO pulse titration were 58% for **Pt/Al$_2$O$_3$**, 35% for **Pt/ZrO$_2$**, 2.5% for **Pt/Nb$_2$O$_5$**, and 12% for **Pt/TiO$_2$**. It should be noted that the SMSI effect resulted in inaccurate estimation of the dispersion of Pt NPs on TiO_2. ICP measurements revealed that the amounts of modified $[Nb_6O_{19}]^{8-}$ were 0.89wt% for **4.0Nb6-Pt/Al$_2$O$_3$**, 1.63% for **4.0Nb6-Pt/ZrO$_2$**, and 1.08wt% for **4.0Nb6-Pt/TiO$_2$**. Considering the dispersion of Pt NPs, $[Nb_6O_{19}]^{8-}$ were modified on the surface of ZrO_2 and TiO_2 supports.

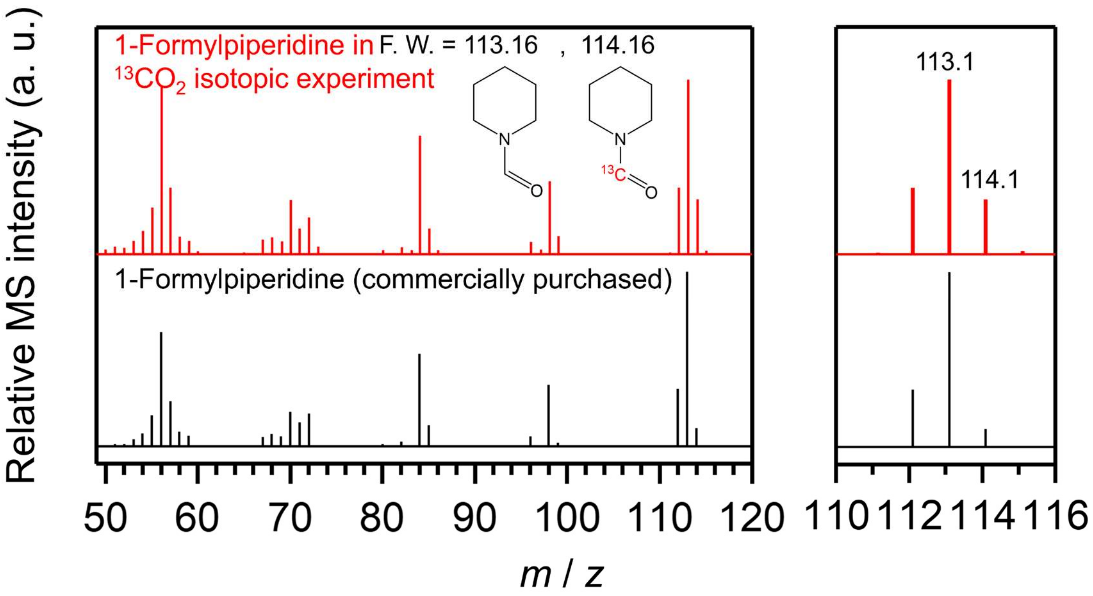

Figure S5. MS profile of peak derived from piperidine in the isotopic experiment using 0.1 MPa of $^{13}CO_2$ with 1.9 MPa of $^{12}CO_2$ and 1.0 MPa of H_2.

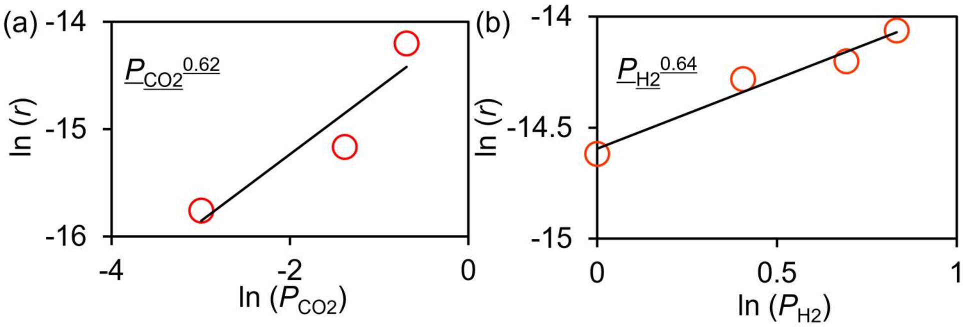

Figure S6. Partial pressure dependence on (a) P_{CO2} and (b) P_{H2} for *N*-formylation reaction of piperidine using CO_2 with **4.0Nb6-Pt/Al$_2$O$_3$**. Reaction conditions: piperidine, 0.1 mmol; methanol, 2 mL; catalyst, 19.5 mg; internal standard, dodecane; CO_2, 0.1–1.0 MPa; H_2, 0.1–2.0 MPa; reaction temperature, 130°C; reaction time, 72 h.