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Supporting Information

Photocatalytic homolysis of methyl formate to dry formaldehyde on PdO/TiO_2: Photocatalytic reverse Tishchenko reaction of methyl formate

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Preparation of $Pd(NH_3)_4Cl_2$ and $Pt(NH_3)_4Cl_2$. $PdCl_2$ and $PtCl_2$ were converted to the corresponding tetramine complex by reacting them with dry ammonia, respectively, according to the known procedure. Typically, 2 g of $PdCl_2$ was introduced into a two-neck round bottomed flask and NH_3 gas was passed through the flask until the dark grey color of $PdCl_2$ changed to white. The same procedure was carried out for the preparation of $Pt(NH_3)_4Cl_2$.

Preparation of $(MO)_n$-TiO_2. Degussa P25 TiO_2 (3 g) and a calculated amount of a metal precursor [$Cu(CH_3COOH)_2.H_2O$: 94 mg, $Pd(NH_3)_4Cl_2$: 69 mg, $Pt(NH_3)_4Cl_2$: 51 mg, $HAuCl_4.xH_2O$: 60 mg] were added into the aqueous solution (40 mL) and subsequently stirred for 2 h. After evaporation of water from the solution by placing the container in an oven (100 °C) for 10 h, the samples were finely ground using a mortar and pestle and subsequently calcined at 400 °C for 4 h in the air. The amount of each metal nanoparticle (M_n) loaded on TiO_2 corresponds to 1% by weight.

Measurements of Methyl Formate/Water (MF/W) Ratios. To measure the M/W ratio of a mixed vapor of methylformate and water being fed into the reactor the vapor was also fed on-line into another GC loaded with Porapak Q column, which can safely separate water from methylformate. The calibration curve for water was obtained by directly injecting 1 μL of each solution having 100, 200 and 500 ppm of water, respectively, in methanol.

GC Analyses. The product stream was introduced on-line into one or two gas chromatographs (GCs) equipped with a flame ionization detector (FID) and a pulsed discharge detector (PDD). Several different types of GC columns were used to quantitatively analyze the products. The types of columns used for the analyses of various products, the oven temperatures, types of detectors, types and flow rates of carrier gases, and the corresponding retention times are listed in Table SI-1.

Table SI-1. Columns used for various products and the operation conditions.

Compounds	Injector Temp (°C)	Injector Type	Column (manufacturer)	Oven	FID	PDD	TCD	Carrier gas	Flow rate (mL min^{-1})	Retention Time (min)
H_2	120	capillary	Carboxen (Supelco)	Programed[1]		o		He	6	1.95
CO	120	capillary	Carboxen (Supelco)	Programed[1]		o		He	6	2.5
CO_2	120	capillary	Carboxen (Supelco)	Programed[1]		o		He	6	9.6
Methane	120	capillary	DB-624 (Agilent)	Programed[1]	o			Ar	5	0.85
Methanol	120	capillary	DB-624 (Agilent)	Programed[1]	o			Ar	5	3.06
Formaldehyde	120	packed	Porapak-N (Agilent)	Isothermal	o			Ar	5	4.74
Methyl formate	120	capillary	DB-624 (Agilent)	Programed[1]	o			Ar	5	3.20
Water	180	packed	Porapak-Q (Agilent)	Isothermal			o	Ar	20	1.34

[1]40 °C for 6 min/5 °C min^{-1}/65 °C for 2 min/20 °C min^{-1}/150 °C for 1 min.

Calibration Curves for GC Analyses. The calibration curves were obtained for the quantitative analyses of the reactants and products. The standard gas mixtures (CH_4: 1012, CO_2: 499, CO: 505, CH_3OH: 496 and H_2: 999 ppm in an Ar balance gas) were purchased from Air Korea. Other standard gas mixtures (CH_3OH: 19.6 ppm in N_2 balance, HCHO: 7 ppm in air balance, $(CH_3)_2O$: 50.2 ppm in Ar balance, and H_2: 1000 and 2000 ppm in Ar balance) were purchased from RIGAS Korea. Formaldehyde, MF, and were calibrated by preparing an aqueous solution of each compound with the concentrations of 100, 200, and 500 ppm, respectively, and injecting 1 μL of each solution into a GC. As an internal standard, methanol was also added into each solution so the concentration of methanol to be matched with that of the compound of interest (100, 200, and 500 ppm, respectively), and the areas of the compound of interest was calibrated with that of methanol.

Measurements of Electron Paramagnetic Resonance Spectra: The EPR spectra were recorded on a Bruker EMX plus spectrometer in the X band CW EPR spectroscopy. All EPR spectra were recorded at 25K with a liquid He temperature control system (ER4112HV). The EPR spectra were measured in the dark and under the irradiation condition with the visible light (light B) or UV light (light D) at a fixed resonance magnetic field. Light B was produced from light A (an AM-1.5 solar simulated light with the spectral width between 320 and 1050 nm) by placing a long-pass 385 nm cut-off filter in front of the light gate to remove the UV part of the solar simulated light. Light D was produced from a Xenon lamp (Max-303, Asahi Japan, wave length = 235-420 nm). The EPR signals became a bit more intense upon shifting light B to light D. All samples were irradiated for 10 minutes. The measurement conditions are as follows:

Temperature = 25 K
Microwave power = 0.9 mW
Microwave frequency = 9.648 (TiO_2), 9.647 (PdO/TiO_2), 9.644 (PdO/TiO_2-MF), and 9.646 (TiO_2-MF) GHz, respectively
Modulation frequency = 100 kHz
Modulation amplitude = 10 G

And the g value was calculated by

$g = h\nu/H\beta$
h= Planck's constant
ν = microwave frequency
H = Applied magnetic field
β = Bohr magneton
h/β = 71.4484

Diffuse Reflectance UV-Vis Spectra. Rigorously dried MO/TiO_2 powders were dried at 200 °C for 5 h under vacuum (10^{-4} Torr) and transferred into a glove box charged with dry Ar. Inside the glove box, 0.5 g of a MO/TiO_2 was loaded into a flat cylindrical fused silica cell (diameter = 19 mm, I.D., thickness = 2 mm, Precision cells inc. US) and 50 μL of methyl formate was introduced into the flat cylindrical cell under the dim red light. The cylindrical cell loaded with MO/TiO_2 and an organic reagent was tightly capped not to allow air goes into the cell. The sample-loaded and tightly-capped cell was wrapped with a piece of black cloth inside the glove box and brought out as such to the atmosphere. The diffuse reflectance spectrum of the sample (kept in the dark) was measured on a UV-vis-NIR spectrometer equipped with an integrating sphere. After obtaining a spectrum, the sample was irradiated with a solar simulated light for a certain period of time, and its diffuse reflectance UV-vis spectrum was taken. The irradiated sample was then exposed to the atmosphere for 10 min and the UV-vis spectrum was taken one more time.

Instrumentation. Diffuse-reflectance UV-vis spectra of the samples were recorded on a Varian Cary 5000 UV-vis-NIR spectrometer equipped with an integrating sphere. Barium sulfate was used as the reference. The diffuse reflectance spectra were converted into the Kubelka-Munk function (K-M). The gas chromatographs were purchased from Young Lin (YL-6000) equipped with a thermal conductivity detector, a flame ionization detector (FID), and a pulsed discharged detector (PDD). Transmission electron microscopy (TEM) images were collected on a JEOL JEM 4010 microscope, The EPR spectra were recorded with a Bruker EMX plus spectrometer in the X band CW EPR spectroscopy.

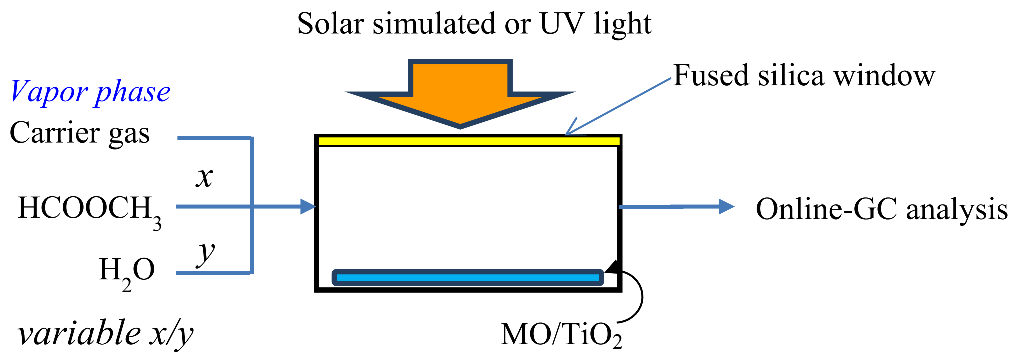

Fig. SI-1: Schematic of the reaction setup.

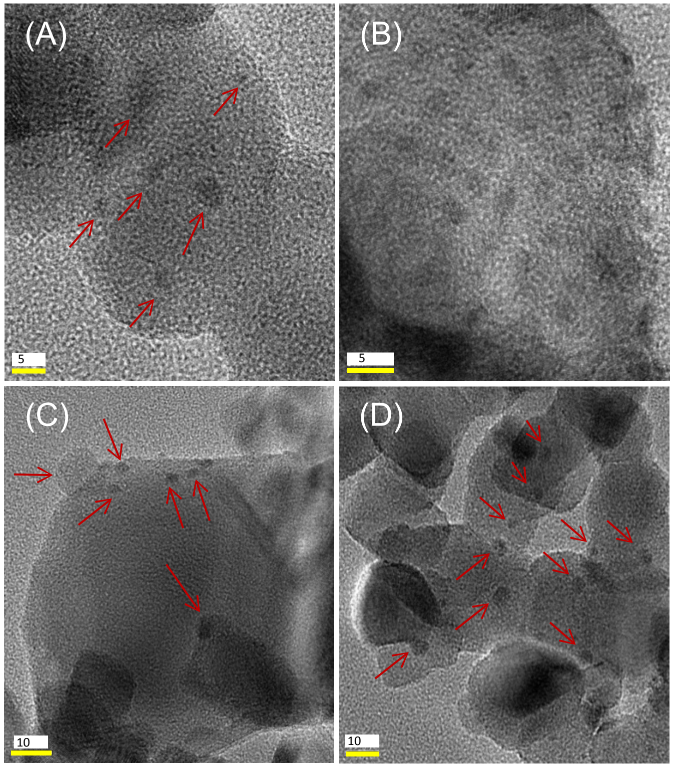

Fig. SI-2. TEM images of $(MO)_n$–TiO_2 showing the $(MO)_n$ particles. A: $(PdO)_n$–TiO_2, B: $(PtO)_n$–TiO_2, C: $(AuO)_n$–TiO_2, D: $(CuO)_n$–TiO_2.

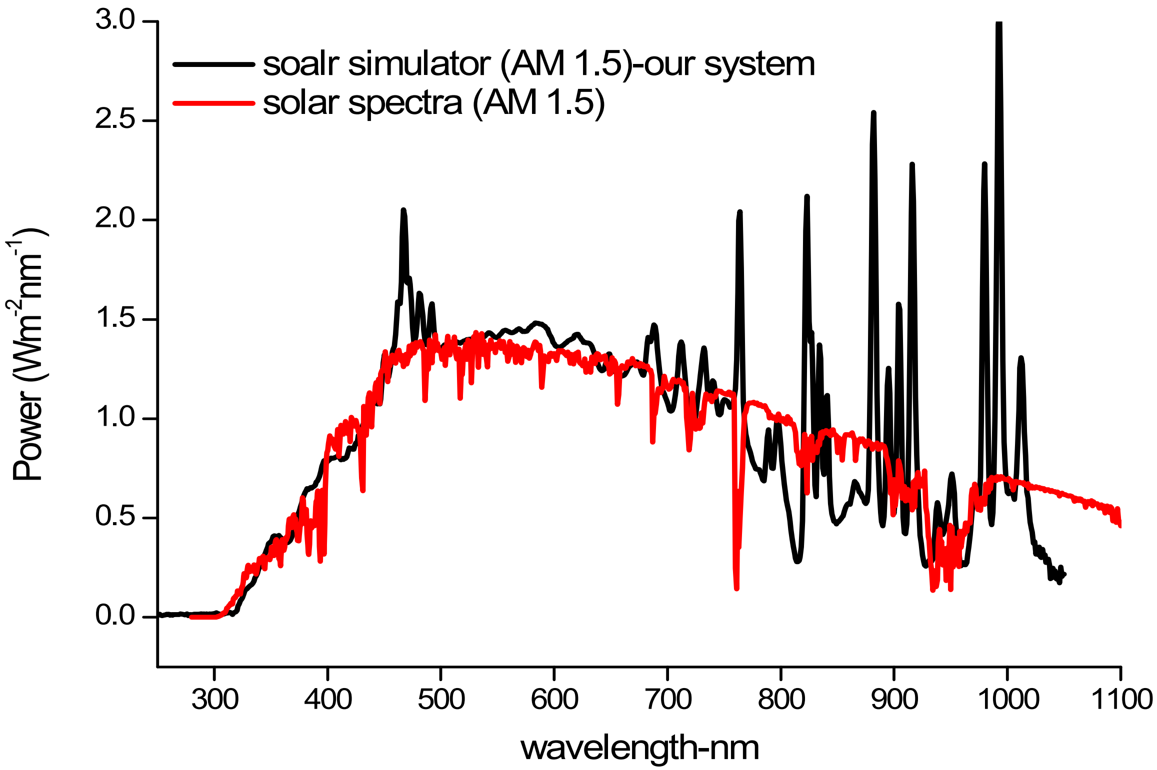

Fig. SI-3. The UV parts of the solar simulated light and the natural solar light both under the AM 1.5 condition.

Table SI-2 Photocatalytic reaction of methyl formate (MF) on $(PdO)_n$-TiO_2 under different conditions.

No.	Co-catalyst	Reactant	Carrier Gas[a]	Input[b]	Reacted[b] (Conv)	H_2	HCHO	DMM[d]	CH_3OH	CO	CO_2	CH_4	Mass balance C %	H %
	Methyl formate/water/methanol, (MF/H_2O = 0.8-1.4)													
1	Pd-TiO_2 (1wt% Pd)	$HCO_2CH_3/H_2O/CH_3OH$	Ar	23.5/ 0.9/ 1.2	3.3 (14.0)	5.65	0.00	0.00	2.20	0.00	4.77	0.19	88	84
2	Pd-TiO_2 (1wt% Pd)	$HCO_2CH_3/H_2O/CH_3OH$	H_2	21.5/ 0.8/ 3.0	2.7 (13.0)	NM[c]	0.00	0.00	3.98	0.03	3.95	0.03	93	-[e]
3	Pd-TiO_2 (1wt% Pd)	$HCO_2CH_3/H_2O/CH_3OH$	O_2	39.6/ 1.4/ 4.2	6.7 (17.0)	0.00	0.00	0.00	5.95	0.02	6.04	0.08	91	-[e]
	Methyl formate/water/methanol, (MF/H_2O = 14-20)													
4	Pd-TiO_2 (1wt% Pd)	$HCO_2CH_3/H_2O/CH_3OH$	Ar	641.0/20.0/10.0	41.0 (6.0)	23.70	43.00 (53)	1.46	9.60	0.40	15.60	0.05	91	91
5	Pd-TiO_2 (1wt% Pd)	$HCO_2CH_3/H_2O/CH_3OH$	H_2	501.0/16.0/14.8	19.0 (4.0)	NM[c]	10.70 (28)	0.95	15.00	0.23	5.90	0.00	91	-[e]
6	Pd-TiO_2 (1wt% Pd)	$HCO_2CH_3/H_2O/CH_3OH$	O_2	437.0/14.0/15.6	20.0 (4.5)	0.00	10.70 (26)	1.49	15.00	0.11	5.90	0.00	90	-[e]
	Methyl formate/no water/methanol, (MF/H_2O = ∞)													
7	$(PdO)_n$-TiO_2 (1wt% Pd)	HCO_2CH_3/CH_3OH	Ar	5.5 / 0.41	1.8/0.07 (32.7)	0.00	2.85 (79)	0.00	0.48	0.02	0.05	0.05	83	82
8	$(PdO)_n$-TiO_2 (1wt% Pd)	HCO_2CH_3/CH_3OH	Ar	27.3 / 1.25	6.5/0.70 (24.9)	0.45	10.90 (84)	0.00	0.51	0.02	0.05	0.05	81	84
9	$(PdO)_n$-TiO_2 (1wt% Pd)[f]	HCO_2CH_3/CH_3OH	Ar	513.0 / 2.80	16.0/0.58 (3.2)	1.32	27.00 (84)	0.00	2.22	0.12	0.05	0.04	85	89
10	$(PdO)_n$-TiO_2 (1wt% Pd)[h]	HCO_2CH_3/CH_3OH	Ar	496.0 / 2.32	8.0/0.54 (1.6)	0.12	15.50 (97)	0.00	1.78	0.00	0.12	0.02	98	98
11	$(PdO)_n$-TiO_2 (1wt% Pd)[i]	HCO_2CH_3/CH_3OH	Ar	475.0 / 2.32	1.5/0.30 (0.3)	0.00	2.58 (86)	0.00	2.02	0.00	0.06	0.02	89	87
12	$(PdO)_n$-TiO_2 (1wt% Pd)[g]	HCO_2CH_3/CH_3OH	Ar	459.0 / 2.42	31.0/0.45 (6.8)	7.20	40.00 (65)	0.00	1.97	6.64	2.72	0.40	81	77
13	$(PdO)_n$-TiO_2 (1wt% Pd)	HCO_2CH_3/CH_3OH	O_2	516.0 / 2.80	20.0/0.30 (3.9)	0.00	33.60 (84)	0.00	2.50	0.18	4.29	0.08	96	-[e]
14	$(PdO)_n$-TiO_2 (1wt% Pd)	HCO_2CH_3/CH_3OH	H_2	516.0 / 2.80	3.6/0.06 (0.7)	NM[c]	9.90 (83)	0.00	2.74	0.16	0.21	0.00	87	-[e]
15	$(PtO)_n$-TiO_2 (1wt% Pd)	HCO_2CH_3/CH_3OH	Ar	543.2 / 2.84	6.2/0.71 (1.1)	0.92	11.00 (89)	0.00	0.69	0.07	0.04	0.04	91	98
16	$(AuO)_n$-TiO_2 (1wt% Pd)	HCO_2CH_3/CH_3OH	Ar	493.0 / 2.98	2.2/0.29 (0.4)	0.18	2.61 (59)	0.00	3.27	0.27	1.00	0.08	88	98
17	$(CuO)_n$-TiO_2 (1wt% Pd)	HCO_2CH_3/CH_3OH	Ar	488.0 / 2.70	2.0/1.22 (0.4)	0.18	1.34 (34)	0.00	3.92	0.37	0.75	0.12	86	104
18	TiO_2	HCO_2CH_3/CH_3OH	Ar	493.0 / 2.80	0.0/0.00 (0.0)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-[e]	-[e]
19	Pd nanoparticles	HCO_2CH_3/CH_3OH	Ar	516.0 / 2.80	2.5/0.70 (0.5)	0.00	4.00 (80)	0.00	1.90	0.00	0.05	0.05	82	82
20	$(PdO)_n$-ZnO (1wt% Pd)	HCO_2CH_3/CH_3OH	Ar	516.0 / 2.90	0.6/0.70 (0.1)	0.00	0.88 (73)	0.00	2.23	0.00	0.02	0.02	84	84
21	$(PdO)_n$-Al_2O_3 (1wt% Pd)	HCO_2CH_3/CH_3OH	Ar	498.0 / 2.70	2.2/0.10 (0.4)	0.00	3.99 (90)	0.00	2.65	0.00	0.00	0.00	92	92
22	$(PdO)_n$-TiO_2 (0.5wt% Pd)	HCO_2CH_3/CH_3OH	Ar	534.0 / 4.40	10.7/0.18 (2.0)	1.88	18.86 (88)	0.00	4.04	0.37	0.03	0.02	92	97
23	$(PdO)_n$-TiO_2 (2wt% Pd)	HCO_2CH_3/CH_3OH	Ar	531.0 / 2.46	14.3/0.56 (2.7)	1.03	22.80 (80)	0.00	1.90	0.55	0.08	0.07	84	84
24	$(PdO)_n$-TiO_2 (3wt% Pd)	HCO_2CH_3/CH_3OH	Ar	538.0 / 3.26	13.0/0.78 (2.4)	1.05	22.41 (86)	0.00	2.48	0.33	0.40	0.08	89	91
25	None	HCO_2CH_3/CH_3OH	Ar	676.0 / 2.84	0.0/0.00	0.00	0.00	0.00	2.84	0.00	0.00	0.00	-[e]	-[e]

[a]Flow rate = 6 mL min^{-1}, [b]In μmol h^{-1} cm^{-2}, [c]NM = not measured, [d]DMM = dimethoxy methane, [e]nc = not calculated, [f]1 Sun condition (light A), [h]385-1050 nm (light B) and [i]515- 1050 nm (light C) and [g]220- 420 nm (light D).

Table SI-3. Thermocatalytic reaction of methyl formate (MF) on $(PdO)_n$-TiO_2 under different conditions.

No.	Co-catalyst	Reactant	Carrier Gas[a]	Input[b]	Reacted[b] (Conv)	H_2	HCHO	DMM[d]	CH_3OH	CO	CO_2	CH_4	Mass balance C %	H %
	Methyl formate/water/methanol, (MF/H_2O = 0.8-1.4), Catalyst													
1	Pd-TiO_2 (1wt% Pd)	$HCO_2CH_3/H_2O/CH_3OH$	Ar	23.5/ 0.9/ 1.23	0.60/-/-	0.00	0.00	0.00	1.23	0.00	0.00	0.04	-[e]	-[e]
2	Pd-TiO_2 (1wt% Pd)	$HCO_2CH_3/H_2O/CH_3OH$	H_2	21.5/ 0.8/ 2.95	1.30/-/-	[c]NM	0.00	0.00	2.95	0.02	0.00	0.03	-[e]	-[e]
3	Pd-TiO_2 (1wt% Pd)	$HCO_2CH_3/H_2O/CH_3OH$	O_2	39.6/ 1.4/ 4.20	2.40/-/-	0.00	0.00	0.00	4.20	0.00	1.09	0.00	-[e]	-[e]
	Methyl formate/water/methanol, (MF/H_2O = 14-20), Catalyst													
4	Pd-TiO_2 (1wt% Pd)	$HCO_2CH_3/H_2O/CH_3OH$	Ar	641.0/20.0/10.00	9.30/-/-	0.00	2.82	1.41	10.00	0.00	3.60	0.00	-[e]	-[e]
5	Pd-TiO_2 (1wt% Pd)	$HCO_2CH_3/H_2O/CH_3OH$	H_2	501.0/16.0/14.80	9.20/-/-	[c]NM	1.00	1.10	14.80	0.12	1.97	0.00	-[e]	-[e]
6	Pd-TiO_2 (1wt% Pd)	$HCO_2CH_3/H_2O/CH_3OH$	O_2	437.0/14.0/15.60	9.90/-/-	0.00	1.00	1.46	15.60	0.11	1.48	0.00	-[e]	-[e]
	Methyl formate/no water/methanol, (MF/H_2O = ∞), Catalyst													
7	$(PdO)_n$-TiO_2(1wt% Pd)	HCO_2CH_3/CH_3OH	Ar	5.5 / 0.41	0.00	0.00	0.00	0.00	0.41	0.00	0.00	0.00	-[e]	-[e]
8	$(PdO)_n$-TiO_2(1wt% Pd)	HCO_2CH_3/CH_3OH	Ar	27.0 / 1.25	0.65/-	0.00	1.30	0.00	1.25	0.00	0.00	0.00	-[e]	-[e]
9	$(PdO)_n$-TiO_2(1wt% Pd)[f]	HCO_2CH_3/CH_3OH	Ar	513.0 / 2.80	0.76/-	0.00	1.52	0.00	2.80	0.00	0.00	0.00	-[e]	-[e]
10	$(PdO)_n$-TiO_2(1wt% Pd)[h]	HCO_2CH_3/CH_3OH	Ar	496.0 / 2.32	0.65/-	0.00	1.12	0.00	2.32	0.00	0.00	0.00	-[e]	-[e]
11	$(PdO)_n$-TiO_2(1wt% Pd)[i]	HCO_2CH_3/CH_3OH	Ar	475.0 / 2.32	0.00/-	0.00	0.00	0.00	2.32	0.00	0.00	0.00	-[e]	-[e]
12	$(PdO)_n$-TiO_2(1wt% Pd)[g]	HCO_2CH_3/CH_3OH	Ar	459.0 / 2.42	0.76/-	0.00	1.20	0.00	2.42	0.00	0.00	0.00	-[e]	-[e]
13	$(PdO)_n$-TiO_2(1wt% Pd)	HCO_2CH_3/CH_3OH	O_2	515.0 / 2.80	1.13/-	0.00	0.76	0.00	2.80	0.02	0.32	0.00	-[e]	-[e]
14	$(PdO)_n$-TiO_2(1wt% Pd)	HCO_2CH_3/CH_3OH	H_2	515.0 / 2.80	2.18/-	[c]NM	0.00	0.00	2.80	0.06	0.04	0.00	-[e]	-[e]
15	$(PtO)_n$-TiO_2 (1wt% Pd)	HCO_2CH_3/CH_3OH	Ar	543.2 / 2.84	0.75/-	0.10	1.31	0.00	2.84	0.00	0.00	0.00	-[e]	-[e]
16	Au-TiO_2 (1wt% Pd)	HCO_2CH_3/CH_3OH	Ar	493.0 / 2.98	0.00/-	0.00	0.00	0.00	2.98	0.00	0.00	0.00	-[e]	-[e]
17	$(CuO)_n$-TiO_2(1wt% Pd)	HCO_2CH_3/CH_3OH	Ar	488.0 / 2.70	0.00/-	0.05	1.23	0.00	2.70	0.00	0.12	0.10	-[e]	-[e]
18	TiO_2	HCO_2CH_3/CH_3OH	Ar	493.0 / 2.80	0.00/-	0.00	0.00	0.00	2.80	0.00	0.00	0.00	-[e]	-[e]
19	$(PdO)_n$	HCO_2CH_3/CH_3OH	Ar	516.0 / 2.80	0.00/-	0.00	0.00	0.00	2.80	0.00	0.00	0.00	-[e]	-[e]
20	$(PdO)_n$-ZnO (1wt% Pd)	HCO_2CH_3/CH_3OH	Ar	516.0 / 2.90	0.02/-	0.00	0.00	0.00	2.23	0.00	0.02	0.02	-[e]	-[e]
21	$(PdO)_n$-Al_2O_3 (1wt% Pd)	HCO_2CH_3/CH_3OH	Ar	498.0 / 2.70	0.02/-	0.00	0.00	0.00	2.65	0.00	0.02	0.02	-[e]	-[e]
22	$(PdO)_n$-TiO_2(0.5wt% Pd)	HCO_2CH_3/CH_3OH	Ar	534.0 / 4.40	0.68/-	0.00	1.32	0.00	4.40	0.00	0.02	0.02	-[e]	-[e]
23	$(PdO)_n$-TiO_2(2wt% Pd)	HCO_2CH_3/CH_3OH	Ar	531.0 / 2.46	0.72/-	0.00	1.44	0.00	2.46	0.00	0.04	0.02	-[e]	-[e]
24	$(PdO)_n$-TiO_2(3wt% Pd)	HCO_2CH_3/CH_3OH	Ar	538.0 / 3.26	0.75/-	0.00	1.38	0.00	3.26	0.00	0.04	0.02	-[e]	-[e]
25	None	HCO_2CH_3/CH_3OH	Ar	676.0 / 1.23	0.00/-	0.00	0.00	0.00	1.23	0.00	0.00	0.00	-[e]	-[e]

[a]Flow rate = 6 mL min^{-1}, [b]In µmol h^{-1} cm^{-2}, [c]NM = not measured, [d]DMM = dimethoxy methane, [e]nc = not calculated, [f]1 Sun condition (light A), [h]385-1050 nm (light B) and [i]515- 1050 nm (light C) and [g]220- 420 nm (light D).