ESI (Electronic Supplementary Information)

Title

Efficient formation of C_3 and C_4 hydrocarbon from cellulose over Pt/Mg-doped ZrO_2 catalysts without hydrogen addition

Authors

Yukino Ofuchi[1], Mihiro Hosokawa[1], Naruki Horie[2], Sae Doi[1], Shuhei Ogo[2], Ayumu Onda[2], Tatsuya Hamaguchi[3], Takafumi Saiki[3], Yasushi Sekine[1]

Affiliations

1 Waseda University, Tokyo, Japan

2 Kochi University, Kochi, Japan

3 Astomos Energy Corporation, Tokyo, Japan

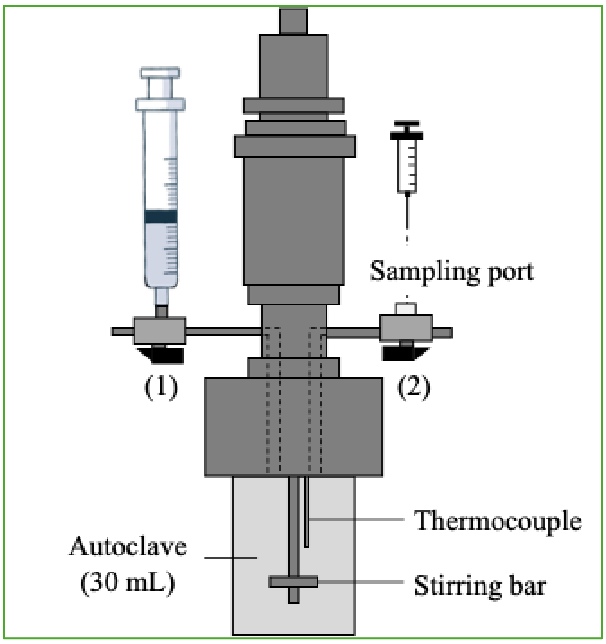


Fig. S1 Schematic diagram of the experimental reactor.

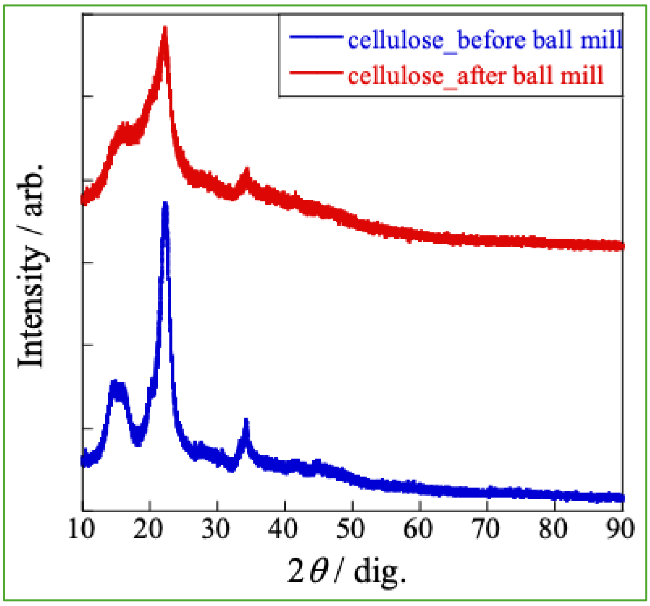


Fig. S2 XRD patters for untreated cellulose and ball-milled one.

Table S1 Physicochemical properties of catalysts in Pt loading change tests.

Catalyst	Metal Dispersion %	Average particle diameter / nm
1wt%Pt/$Zr_{0.5}Mg_{0.5}O_{2-\delta}$	22.0	5.1
3wt%Pt/$Zr_{0.5}Mg_{0.5}O_{2-\delta}$	16.2	7.0
5wt%Pt/$Zr_{0.5}Mg_{0.5}O_{2-\delta}$	13.4	8.4
10wt%Pt/$Zr_{0.5}Mg_{0.5}O_{2-\delta}$	12.7	8.9

Table S2 Specific surface area of catalysts.

Catalyst	Specific surface area / m^2 g^{-1}
1wt%Pt/ZrO_2	68.0
1wt%Pt/$Zr_{0.9}Mg_{0.1}O_{2-\delta}$	51.3
1wt%Pt/$Zr_{0.7}Mg_{0.3}O_{2-\delta}$	70.4
1wt%Pt/$Zr_{0.5}Mg_{0.5}O_{2-\delta}$	70.9
1wt%Pt/MgO	54.5
0.1wt%Pt/$Zr_{0.5}Mg_{0.5}O_{2-\delta}$	76.8
3wt%Pt/$Zr_{0.5}Mg_{0.5}O_{2-\delta}$	51.5
5wt%Pt/$Zr_{0.5}Mg_{0.5}O_{2-\delta}$	50.5
10wt%Pt/$Zr_{0.5}Mg_{0.5}O_{2-\delta}$	73.8
1wt%Pt/$Zr_{0.5}Ca_{0.5}O_{2-\delta}$	37.9
1wt%Pt/$Zr_{0.5}Sr_{0.5}O_{2-\delta}$	37.8
1wt%Pd/$Zr_{0.5}Mg_{0.5}O_{2-\delta}$	70.7
1wt%Ru/$Zr_{0.5}Mg_{0.5}O_{2-\delta}$	74.8

Table S3 Amount of metal in 1wt%Pt/$Zr_{0.5}Mg_{0.5}O_{2-\delta}$ calculated from ICP-OES.

metal	Theoretical loading amount / wt%	Calculated loading amount / wt%
Pt	1	0.66
Zr	55.2	49.7
Mg	14.7	13.9

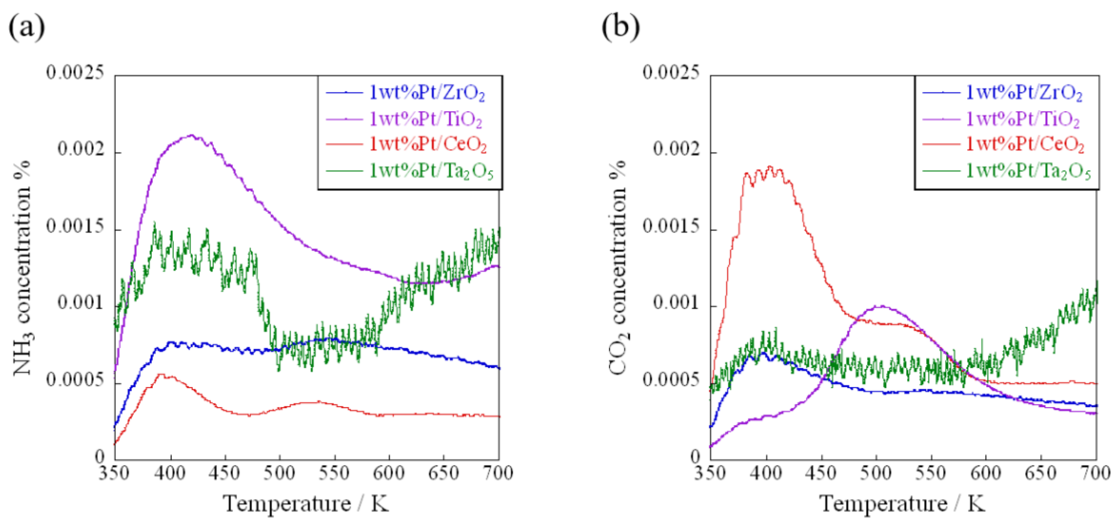


Fig. S3. (a) NH_3 TPD (b) CO_2 TPD profiles of 1wt%Pt/support (TiO_2, ZrO_2, Ta_2O_5, CeO_2).

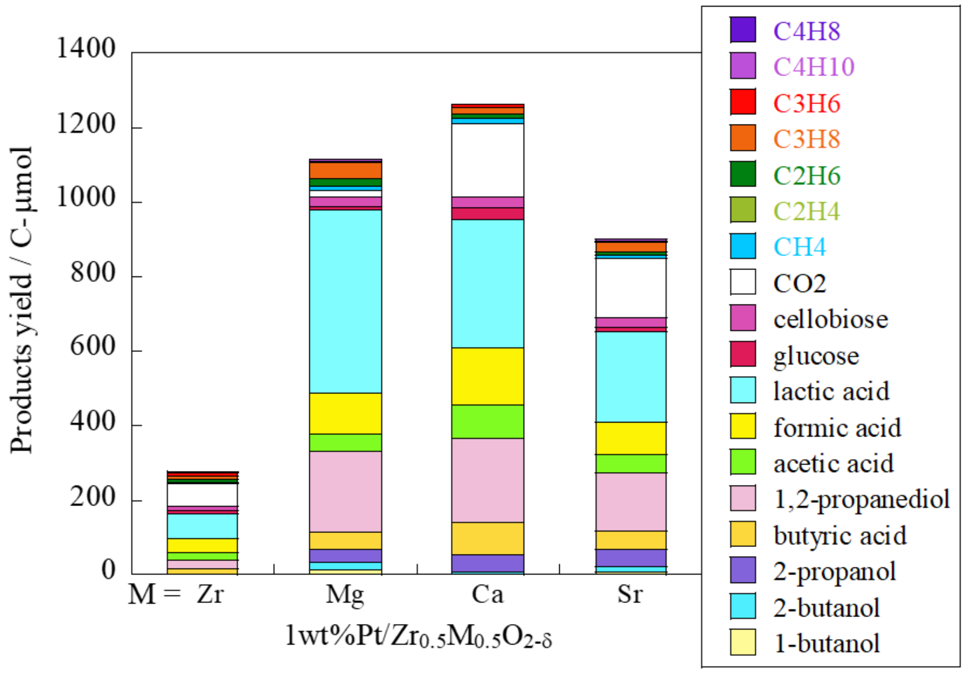
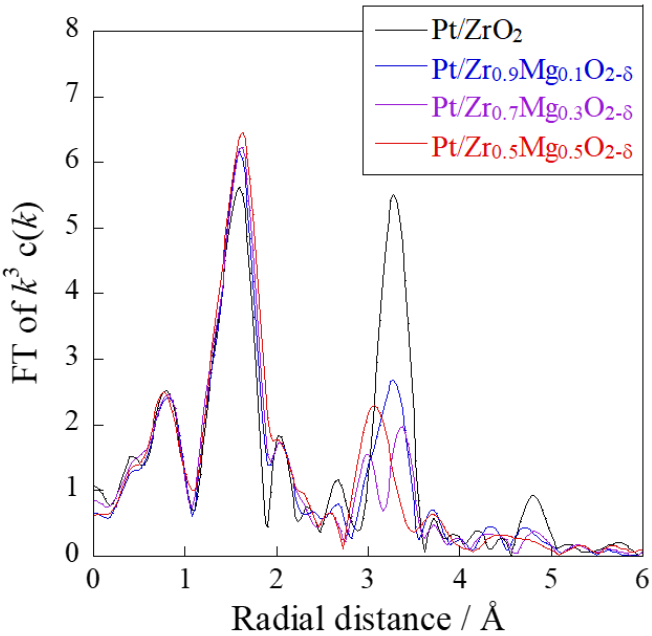


Fig. S4. The liquid products yield using 1wt%Pt/$Zr_{0.5}M_{0.5}O_{2-\delta}$ (M = Zr, Mg, Ca, Sr), cellulose, 443 K, 12 h.



catalyst	Radial distance of Zr-O / Å	Coordination number of Zr-O	Radial distance of Zr-Zr or Zr-Mg / Å	Coordination number of Zr-Zr or Zr-Mg
1wt%Pt/ZrO_2	2.06	3.42	3.63	5.28
1wt%Pt/$Zr_{0.9}Mg_{0.1}O_{2+\delta}$	2.08	3.86	3.61	8.25
1wt%Pt/$Zr_{0.7}Mg_{0.3}O_{2+\delta}$	2.09	4.21	3.41, 3.65	4.93, 3.56
1wt%Pt/$Zr_{0.5}Mg_{0.5}O_{2+\delta}$	2.10	4.89	3.46	9.679

Fig. S5. Fourier transform of EXAFS oscillations of 1wt%Pt/$Zr_{1-x}Mg_xO_{2-\delta}$ (x = 0, 0.1, 0.3, 0.5).

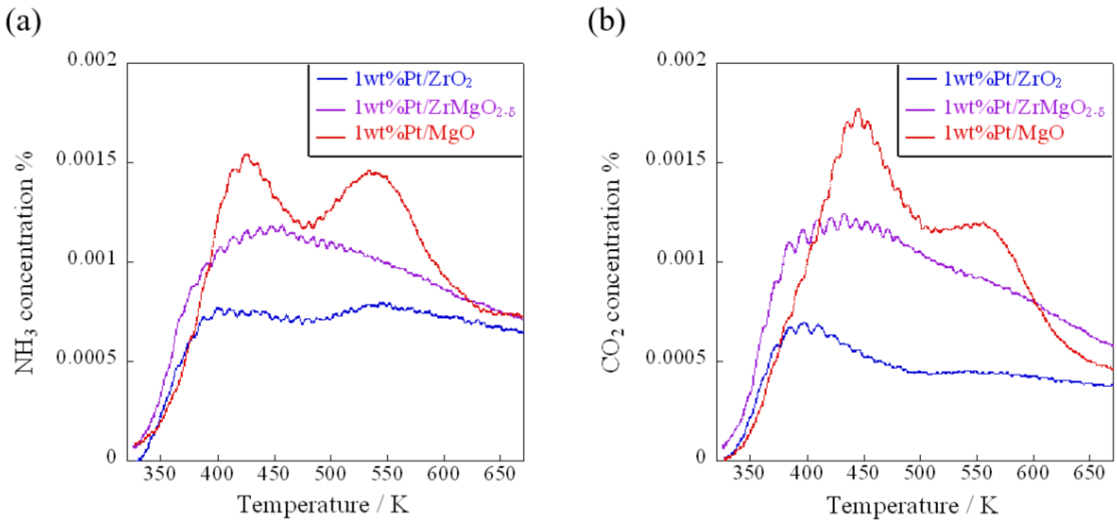


Fig. S6. (a) NH_3 TPD (b) CO_2 TPD profiles of 1wt%Pt/support (ZrO_2, MgO, doped).

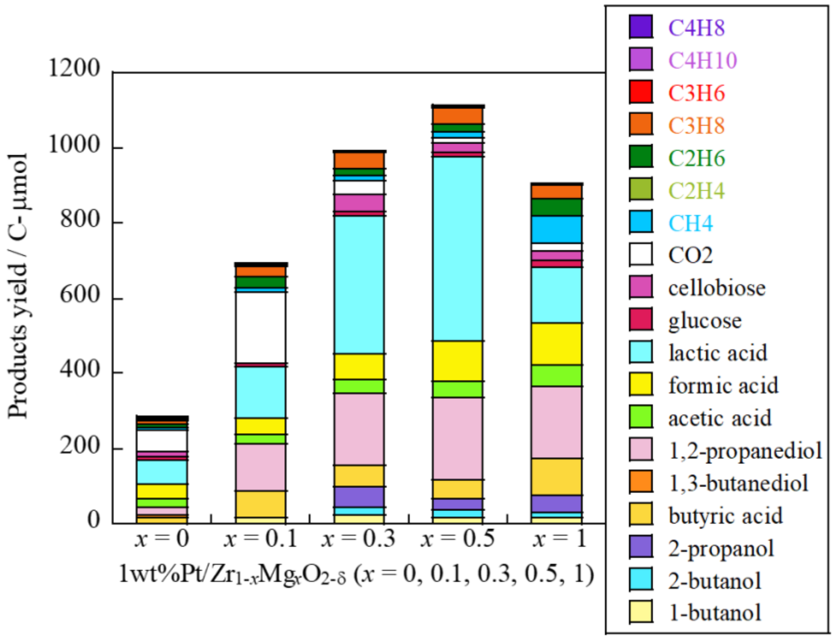


Fig. S7. The liquid products yield using 1wt%Pt/$Zr_{1-x}Mg_xO_{2-\delta}$ (x = 0, 0.1, 0.3, 0.5, 1), cellulose, 443 K, 12 h.

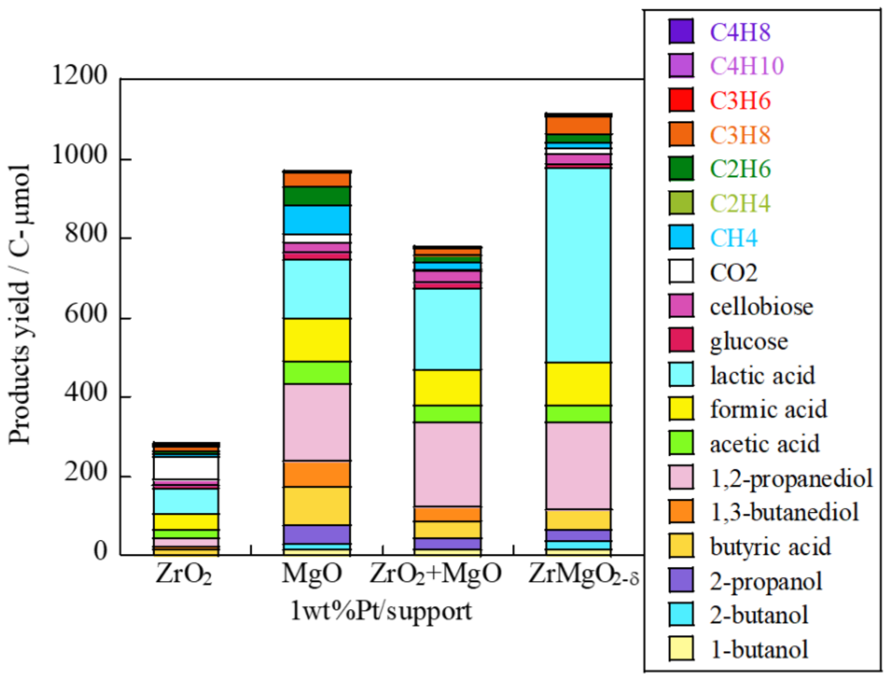


Fig. S8. The liquid products yield using 1wt%Pt/support (ZrO_2, MgO, mixed, doped), cellulose, 443 K, 12 h.

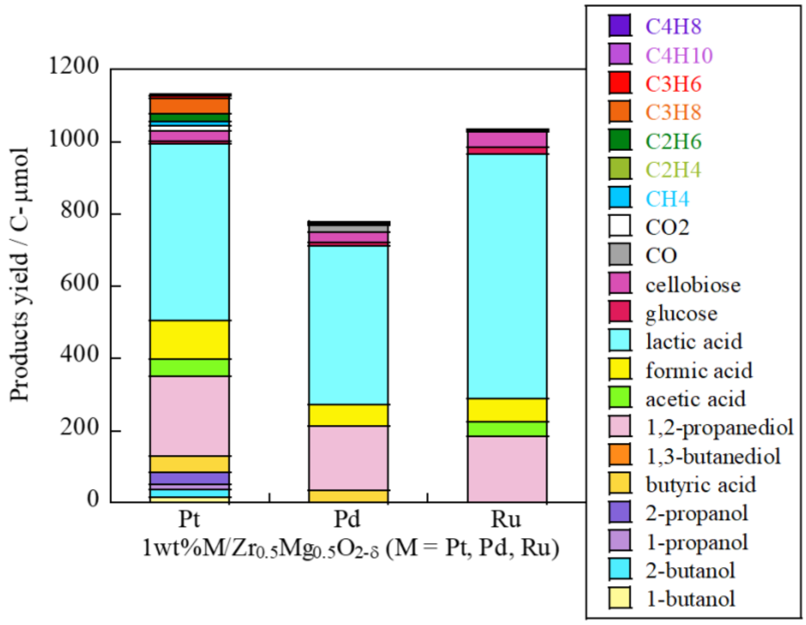


Fig. S9. The liquid products yield using 1wt%M/$Zr_{0.5}Mg_{0.5}O_{2-\delta}$ (M = Pt, Pd, Ru), cellulose, 443 K, 12 h.

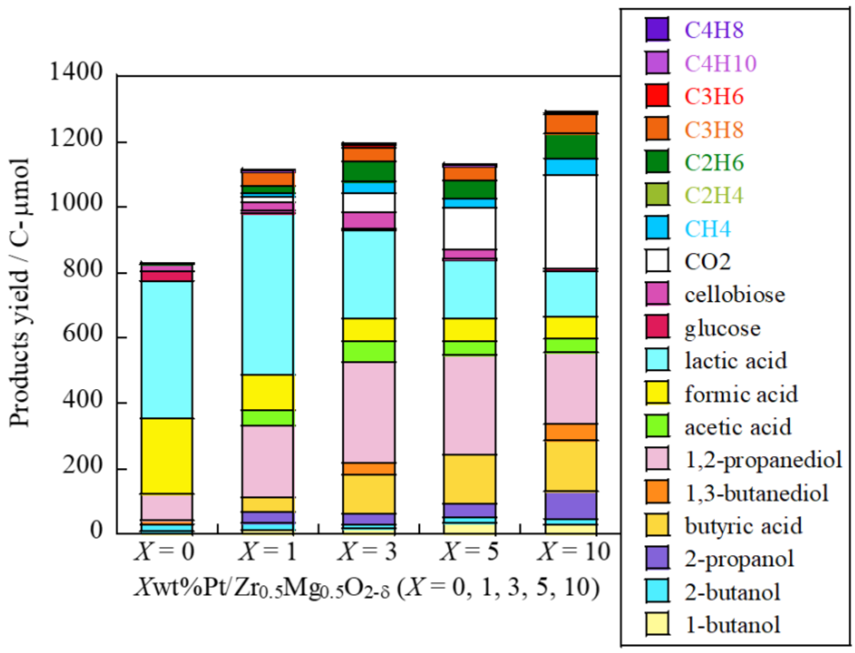
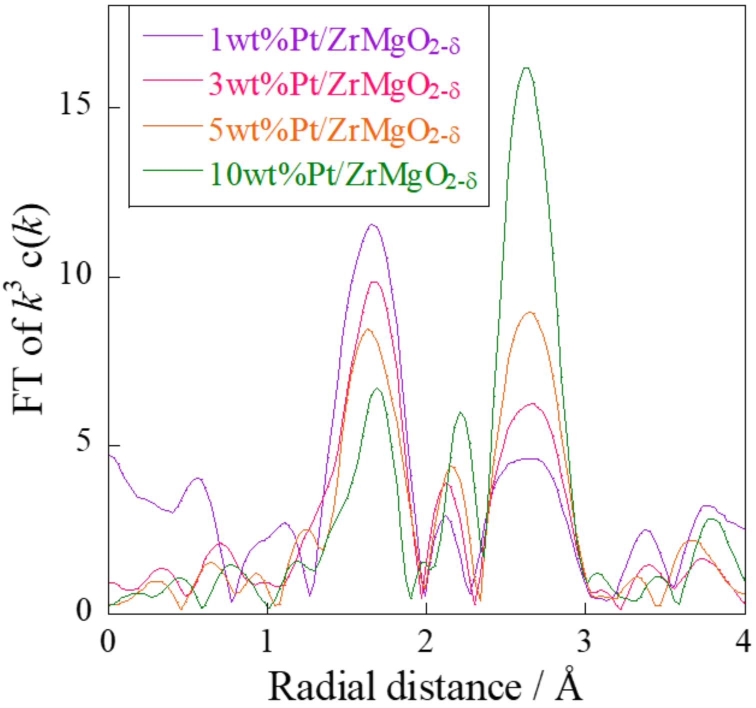


Fig. S10. The liquid products yield using *X*wt%Pt/$Zr_{0.5}Mg_{0.5}O_{2-\delta}$ (*X* =0, 1, 3, 5, 10), cellulose, 443 K, 12 h.



catalyst	Radial distance of Pt-O / Å	Coordination number of Pt-O	Radial distance of Pt-Pt / Å	Coordination number of Pt-Pt / Å
1wt%Pt/ZrO_2	2.01	3.27	2.78	4.13
1wt%Pt/$Zr_{0.5}Mg_{0.5}O_{2-\delta}$	2.00	5.47	2.75	3.03
1wt%Pt/MgO	2.03	4.00	2.79	3.47
3wt%Pt/$Zr_{0.5}Mg_{0.5}O_{2-\delta}$	2.01	4.03	2.76	3.05
5wt%Pt/$Zr_{0.5}Mg_{0.5}O_{2-\delta}$	2.01	3.67	2.76	4.36
10wt%Pt/$Zr_{0.5}Mg_{0.5}O_{2-\delta}$	2.01	2.56	2.76	6.75

Fig. S11. Fourier transform of EXAFS oscillations of *X*wt%Pt/$Zr_{0.5}Mg_{0.5}O_{2-\delta}$ (*X* = 1, 3, 5, 10).

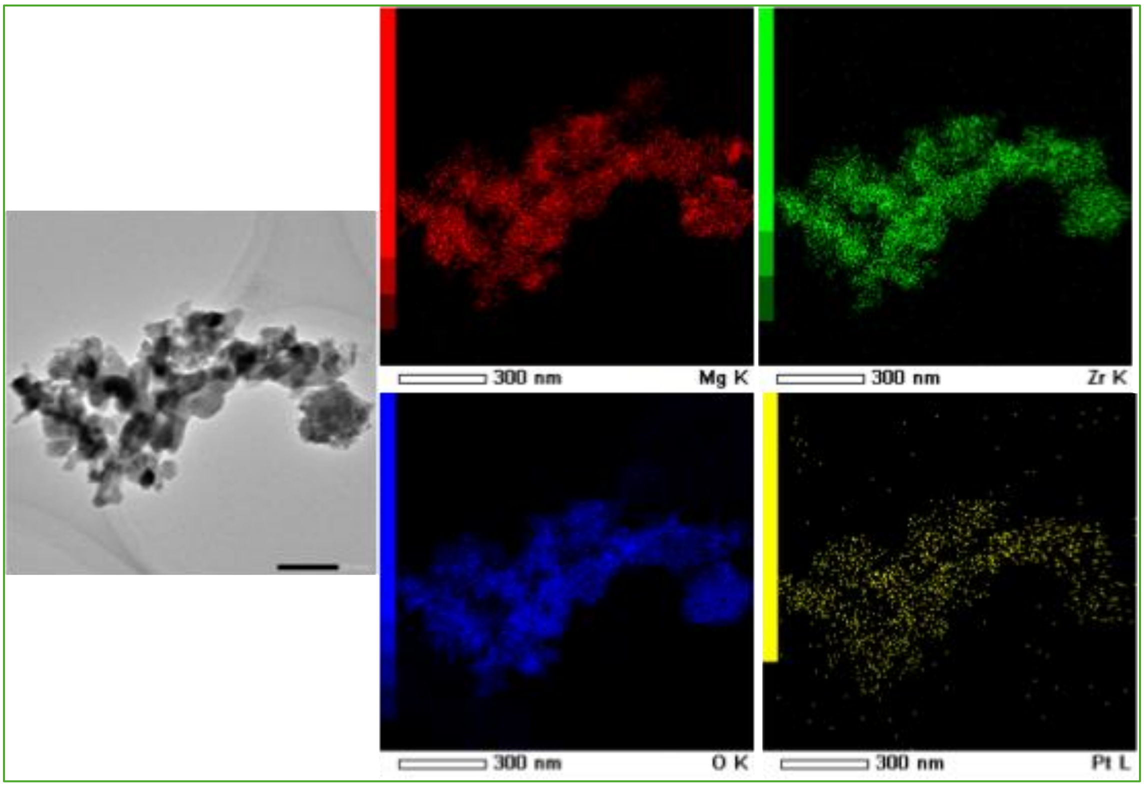


Fig. S12. TEM image and EDS mapping for 1wt%Pt/$Zr_{0.5}Mg_{0.5}O_{2-\delta}$ (x50k).

Table S4 Results of reaction condition change tests using 1wt%Pt/$Zr_{0.5}Mg_{0.5}O_{2-\delta}$.

Cellulose	Water	Pressure (r.t.)	Time	Temp.	Conv.	C_3+C_4 yield	C_3+C_4 selectivity	H_2	C_4	C_3	C_2	CH_4	CO_2	C in liquid
/ g	/ mL	/ atm	/ h	/ K	/ %	/ %	in gas / %	/ μmol	/ μmol	/ μmol	/ μmol	/ μmol	/ μmol	/ μmol
0.25	20	1	12	443	29.7	0.352	65.2	445	2.49	29.8	10.0	7.3	0.0	3444
0.25	20	1	12	453	49.0	0.546	59.6	398	3.96	46.5	20.0	14.2	0.0	2351
0.25	20	1	12	463	39.3	0.697	56.6	436	6.24	58.2	22.2	16.6	10.6	2927
0.25	20	1	12	473	51.6	0.820	16.7	641	10.35	65.5	23.4	26.1	328.5	3062
0.25	20	1	12	483	72.5	1.041	21.6	560	16.71	79.6	29.5	28.5	291.9	5617
0.25	20	1	12	493	84.4	1.590	15.1	1619	23.21	123.9	43.9	54.1	729.7	4894
0.25	20	1	48	443	52.4	0.422	26.9	392	4.19	34.7	13.2	17.5	75.6	3038
0.25	20	1	96	443	63.6	0.593	33.7	363	7.22	47.6	16.5	20.4	70.9	3837
0.25	20	1	168	443	82.0	1.107	24.3	549	12.15	90.3	39.0	27.4	252.8	5192
0.25	20	1	12	443	46.6	0.570	61.1	403	4.22	47.9	21.5	12.0	0.0	3444
0.25	20	1.5	12	443	37.2	0.480	60.8	149	2.78	41.6	20.3	8.3	0.0	2270
0.25	20	2.5	12	443	33.8	0.344	62.7	185	3.01	28.8	12.6	6.4	0.0	2101
0.25	25	1	12	443	39.2	0.287	68.3	111	2.61	23.7	7.6	2.7	2.1	7451
0.25	20	1	12	443	30.7	0.404	65.9	160	2.90	34.1	11.1	3.7	4.5	3165
0.25	15	1	12	443	45.7	0.510	60.4	184	4.84	42.1	15.0	4.4	11.5	2681
0.05	25	1	12	443	23.4	0.686	38.2	112	1.14	11.5	10.1	6.5	3.9	1461
0.05	20	1	12	443	70.8	0.798	38.2	129	1.11	13.6	17.1	4.8	2.0	1243
0.05	15	1	12	443	45.7	0.952	39.7	140	1.69	15.9	12.0	5.0	9.7	957

Table S5 Amount of Mg eluted from catalyst and Mg ions in solution after reaction.

Type of Mg	weight / g
Mg elution from catalyst	0.00727
Amount of Mg ion dissolved in solution after reaction	0.00715

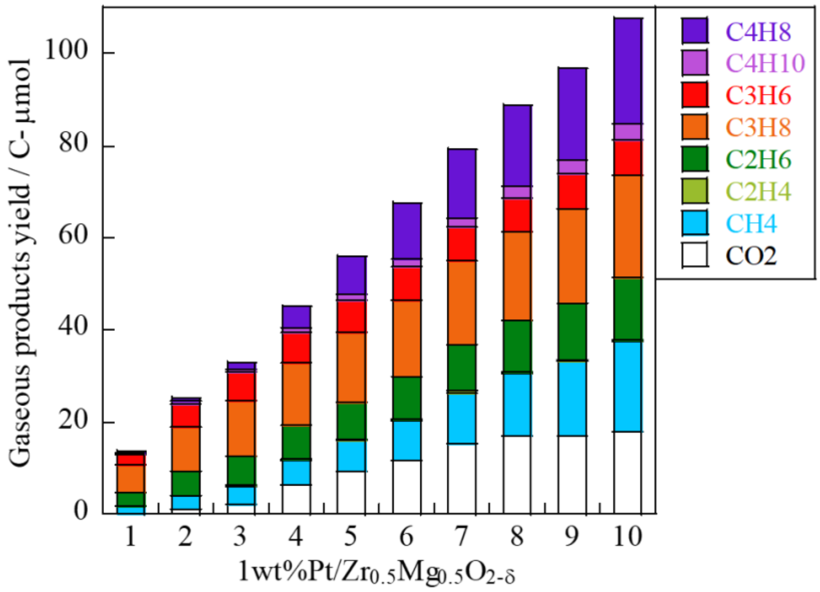


Fig. S13. The gaseous products yield using 1wt%Pt/$Zr_{0.5}Mg_{0.5}O_{2-\delta}$, cellulose 0.05 g, 453 K, 12 h x 10.

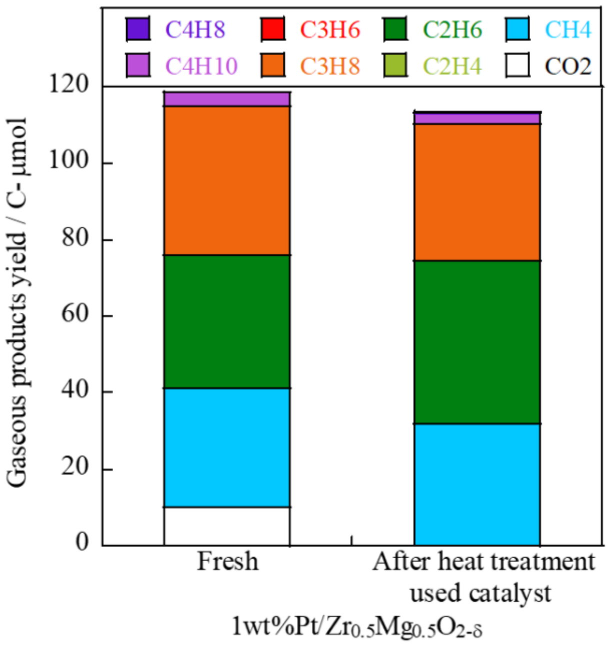


Fig. S14. The gaseous products yield using fresh and after heat treatment used 1wt%Pt/$Zr_{0.5}Mg_{0.5}O_{2-\delta}$, cellulose, 443 K, 24 h.

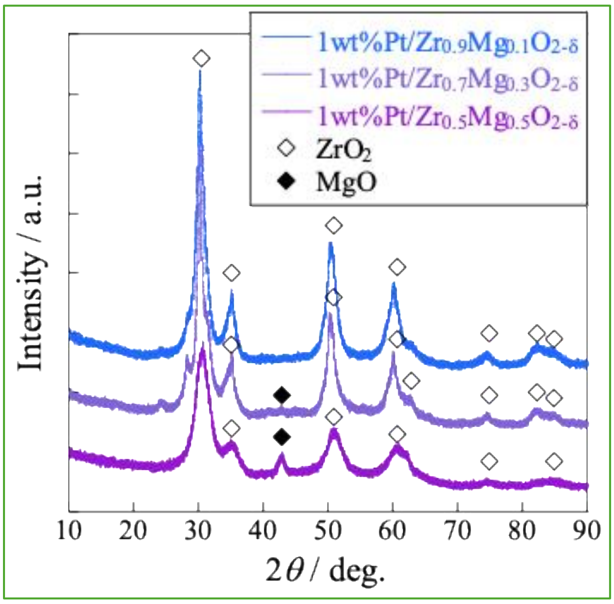


Fig. S15. XRD pattern for 1wt%Pt/$Zr_{1-x}Mg_xO_{2-\delta}$ (x = 0.1, 0.3, 0.5).

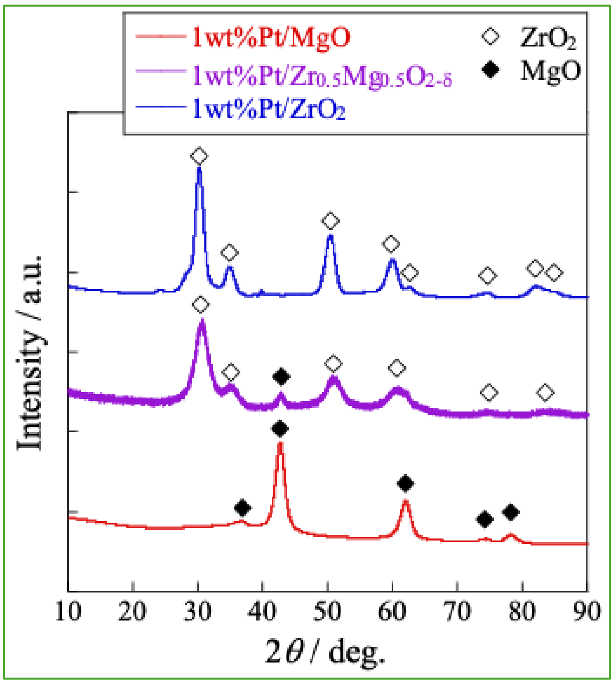


Fig. S16. XRD pattern for 1wt%Pt/$Zr_{1-x}Mg_xO_{2-\delta}$ (x = 0, 0.5, 1).

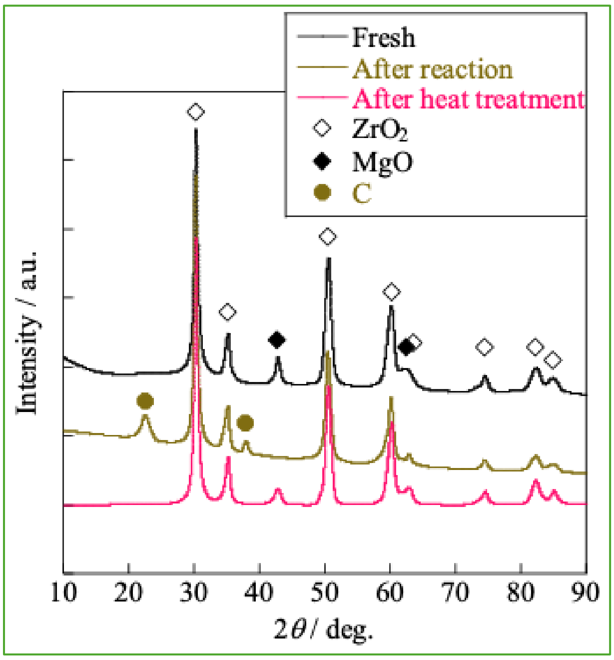


Fig. S17. XRD pattern for 1wt%Pt/$Zr_{0.5}Mg_{0.5}O_{2-\delta}$ (fresh, after reaction, after heat treatment).

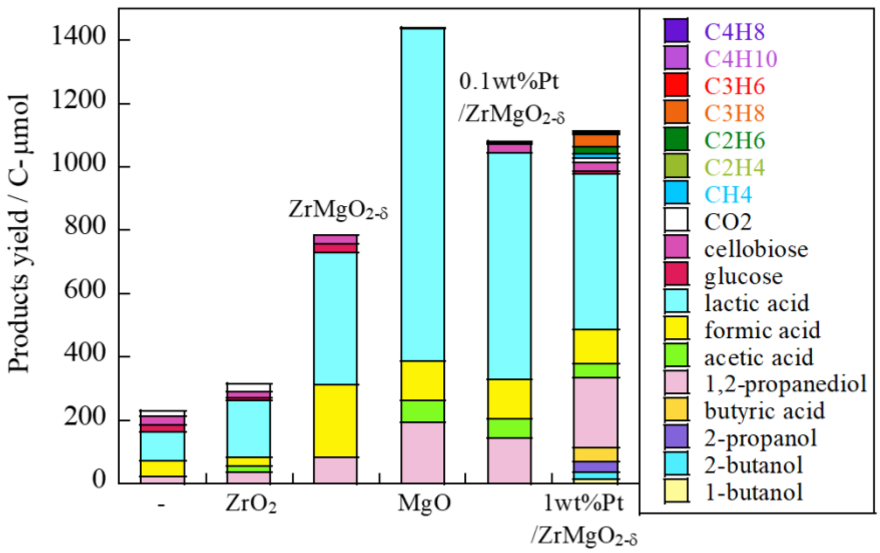


Fig. S18. Gaseous and liquid products yield using *X*wt%Pt/$Zr_{1-x}Mg_xO_{2-\delta}$ (X = 0, 0.1, 1) (x = 0, 0.5, 1), cellulose, 443 K, 12 h.