COMMUNICATION

Electronic Supplementary Information

Superior Catalytic Performance of Intermetallic $CaPt_2$ Nanoparticles Supported on Titanium Group Oxides in Hydrogenation of Ketones to Alcohols

Yasukazu Kobayashi,[*a] Shohei Tada [b], Masaru Kondo [b], Kakeru Fujiwara [c] and Hiroshi Mizoguchi [d]

[a.] *Interdisciplinary Research Center for Catalytic Chemistry, National Institute of Advanced Industrial Science and Technology (AIST), 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan. E-mail: yasu-kobayashi@aist.go.jp.*

[b.] *Department of Materials Science and Engineering, Ibaraki University, 4-12-1 Nakanarusawacho, Hitachi, Ibaraki 316-8511, Japan.*

[c.] *Department of Chemistry and Chemical Engineering, Yamagata University, 4-3-16 Jonan, Yonezawa-shi, Yamagata 992-8510, Japan.*

[d.] *International Center for Materials Nanoarchitectonics (WPI-MANA), National Institute for Materials Science (NIMS), Tsukuba, Ibaraki 305-0044, Japan.*

1. Experimental

1.1. Density functional theory (DFT) periodic calculations

It was performed using the generalized gradient approximation, Perdew–Burke–Ernzerhof functional[1], and the projected augmented plane wave method[2] implemented in the Vienna *Ab initio* simulation package (VASP)[3]. An energy cutoff of 600 eV and a 10 × 10 × 10 gamma-centered *k*-mesh were used. A Wigner–Seitz radius of 0.146 nm was used for the site projections of all the atoms. The atomic charges were estimated by Bader charge analysis[4], and the crystal structures were visualized using the VESTA code[5].

1.2. Characterization for the prepared samples

The crystal structures were investigated by X-ray diffraction (XRD, MiniFlex 600, Rigaku) with CuKα radiation generated at 40 kV and 15 mA. The porosity was examined by N_2 adsorption at −196 °C (BELLSORP mini-II, Microtrac-BEL). Before the measurement, the sample powder was pretreated at 150 °C for 30 min under a vacuum, and the contained water was removed. The morphology was observed by scanning electron microscopy (SEM, JSM-7000F, JEOL Ltd) and transmission electron microscopy (TEM, JEM-2100F, JEOL Ltd) with energy dispersive X-ray spectrometry (EDX) for elemental analysis. The molar ratio of Ca, Pt and Ti in $CaPt_2/TiO_x$ was analyzed via X-ray fluorescence spectrometry (XRF, Rigaku, ZSX Primus II) at 50 kV and 60 mA.

1.3. Catalyst tests

Hydrogenation of cyclohexanone (0.15 mL, 1.45 mmol) using 5wt% of catalyst was performed in a batch reactor with 0.2 M solution in methanol (7.3 mL) at room temperature and 1 atm H_2 for 16 h. A commercial 3wt%Pt/C (54% water, Wako Pure Chem. Corp.) was used as reference. The turnover frequency (TOF) was calculated to compare the intrinsic catalytic performances based on the surface Pt site for 3wt%Pt/C and $CaPt_2/TiO_x$. The number of surface Pt sites was estimated from CO chemisorption experiments. After the catalyst was reduced at 300 °C under 5%H_2/Ar flow at 50 mL/min for 1 h, several 10%CO/He pulses were dosed into the reduced catalyst at 40 °C to measure the adsorbed CO amount.

References

1. J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865.
2. P. E. Blöchl, Phys. Rev. B: Condens. *Matter Mater. Phys.*, 1994, **50**, 17953.
3. G. Kresse and J. Furthmüller, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1996, **54**, 11169.
4. E. Sanville, S. Kenny, R. Smith and G. Henkelman, *J. Comput. Chem.*, 2007, **28**, 899.
5. K. Momma and F. Izumi, *J. Appl. Crystallogr.*, 2011, **44**, 1272.

Table S1 Summary of the results of XRD, N_2 adsorption, XRF, SEM-/TEM-EDX for $CaPt_2$ supported on TiO_x, ZrO_x and HfO_x.

Sample	XRD measurements			N_2 adsorption		XRF			SEM-/TEM-EDX							
	D[a]	Lattice constant [Å]		SA	Vp	Molar ratio [mol%]			Measurement		Average molar ratio [mol%]				Pt/Ca[b]	O/Ti[b]
	[nm]	Exp.	ICSD value	[m^2/g]	[cm^3/g]	Ca	Pt	Ti			Ca	Pt	Ti, Zr or Hf	O	[mol/mol]	[mol/mol]
$CaPt_2/TiO_x$	70	7.552	7.598	32	0.02	12	29	59	SEM		4.4	12.4	13.9	69.6	3	-
									TEM	Pt-rich position	14.7	59.5	11.4	14.4	4.3	3.1
										Ti-rich position	1.7	0.3	43.9	54.1	0.2	1.3
$CaPt_2/ZrO_x$	60	7.565		-	-	-			SEM		8.1	18.4	1.3	72.2	3.3	-
$CaPt_2/HfO_x$	60	7.573		-	-	-			SEM		3.5	35	14.7	46.8	10.1	-

a) Crystallite sizes were calculated by the Scherrer equation with a main peak at 2θ=20.3°.

b) Average Pt/Ca and O/Ti molar ratios were calculated from a set of data described in **Table S2**.

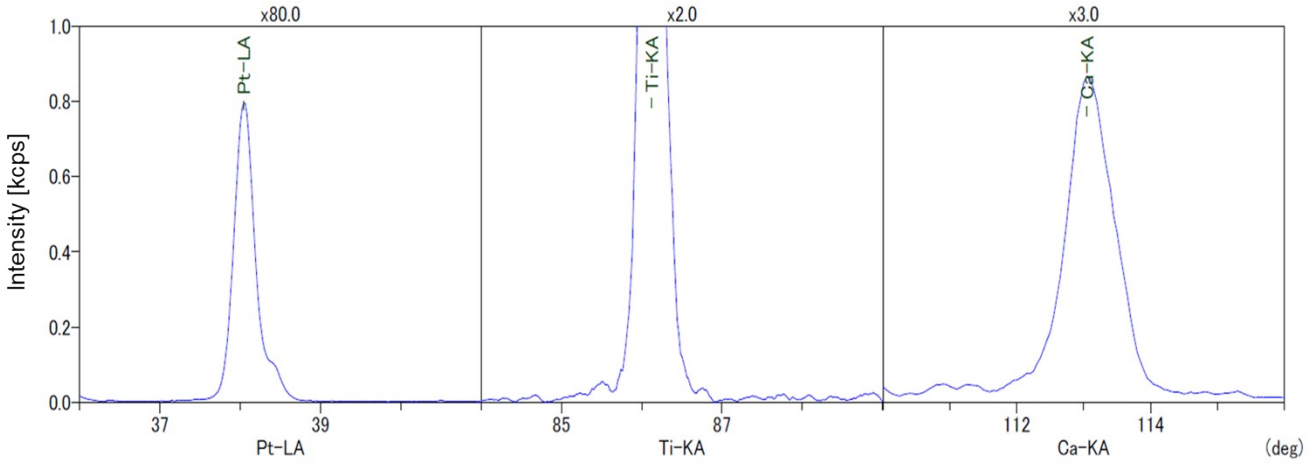

Fig. S1 Spectra of Pt, Ti and Ca elements measured by XRF.

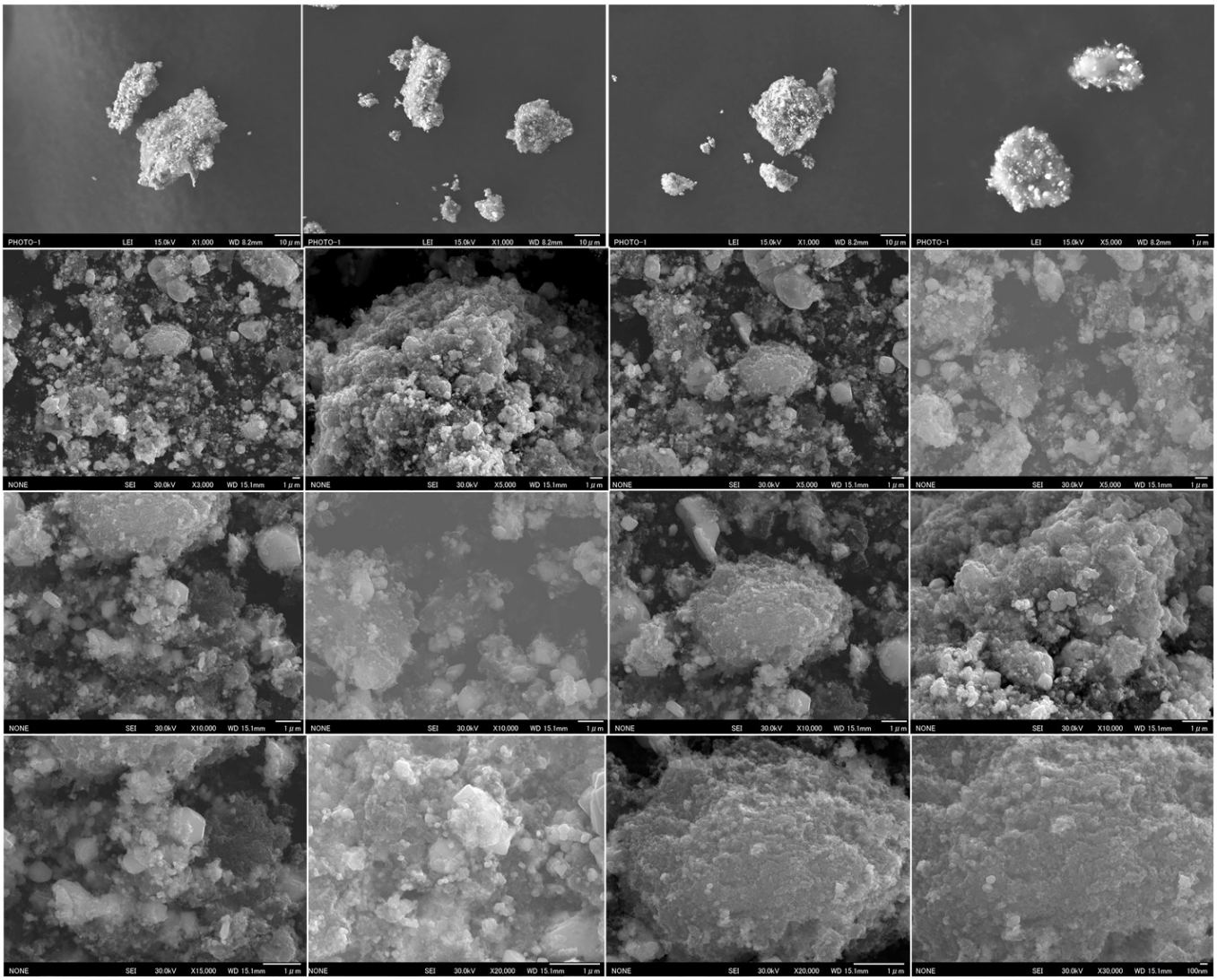

Fig. S2 SEM images of $CaPt_2/TiO_x$.

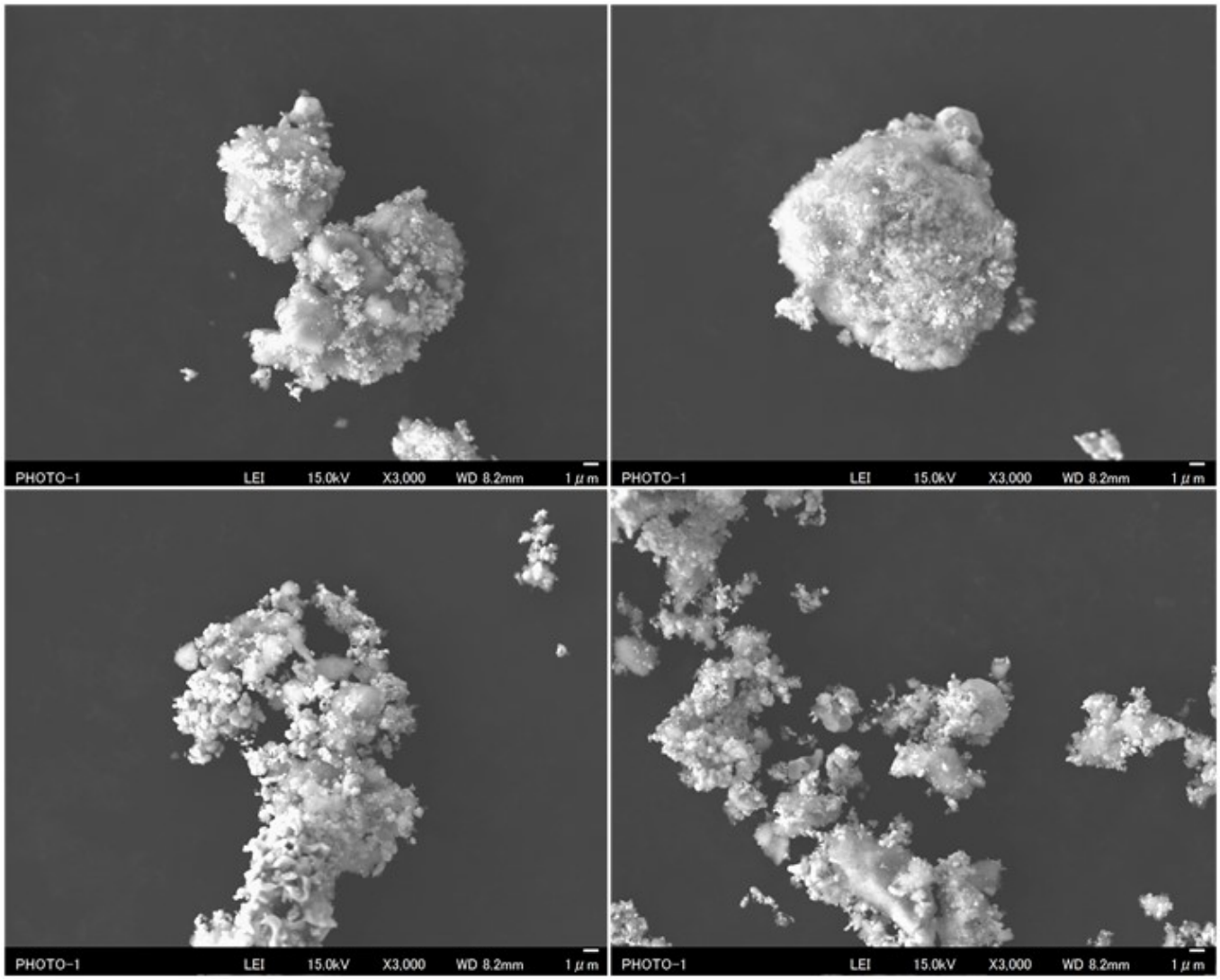

Fig. S3 SEM images of $CaPt_2/ZrO_x$.

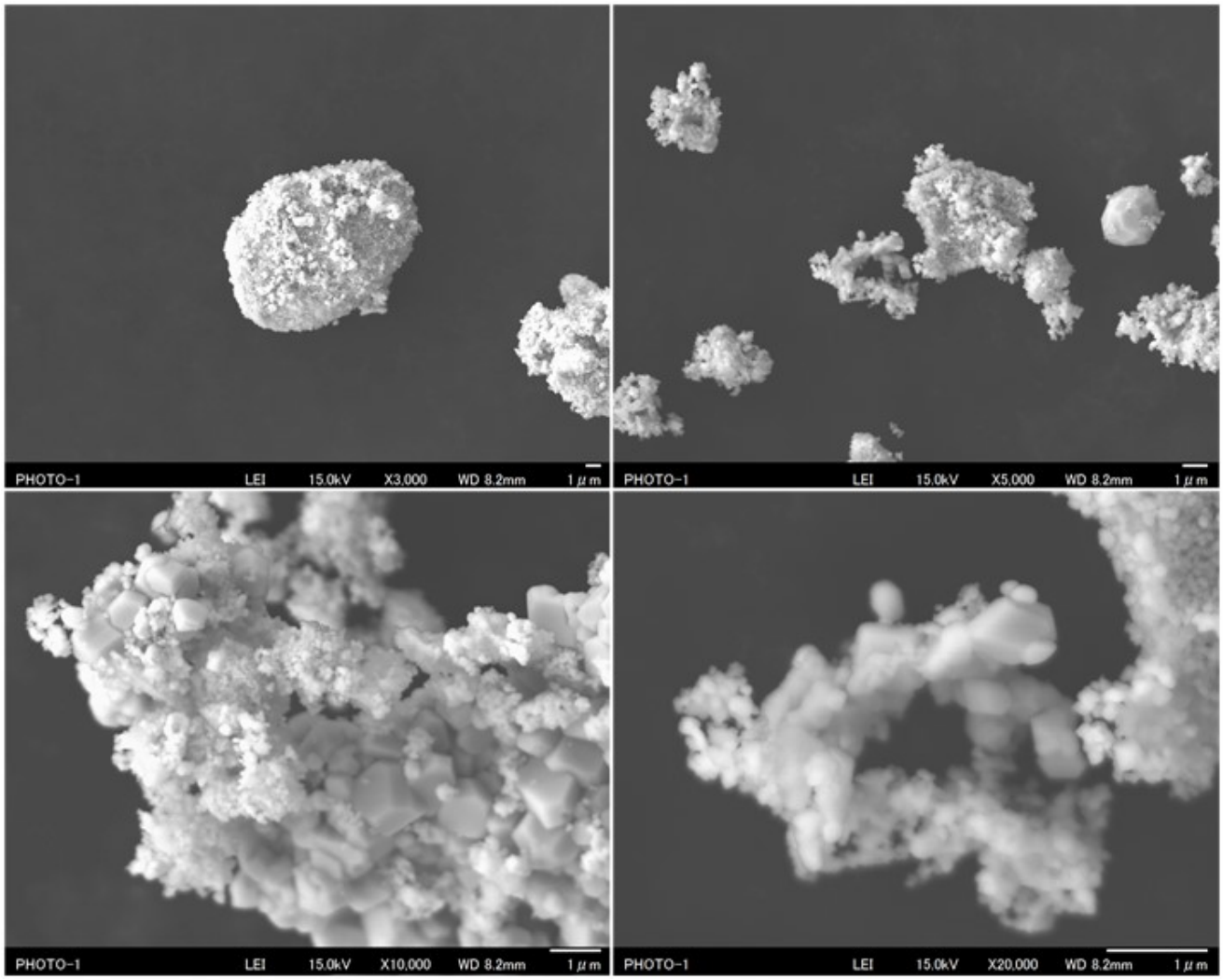

Fig. S4 SEM images of $CaPt_2/HfO_x$.

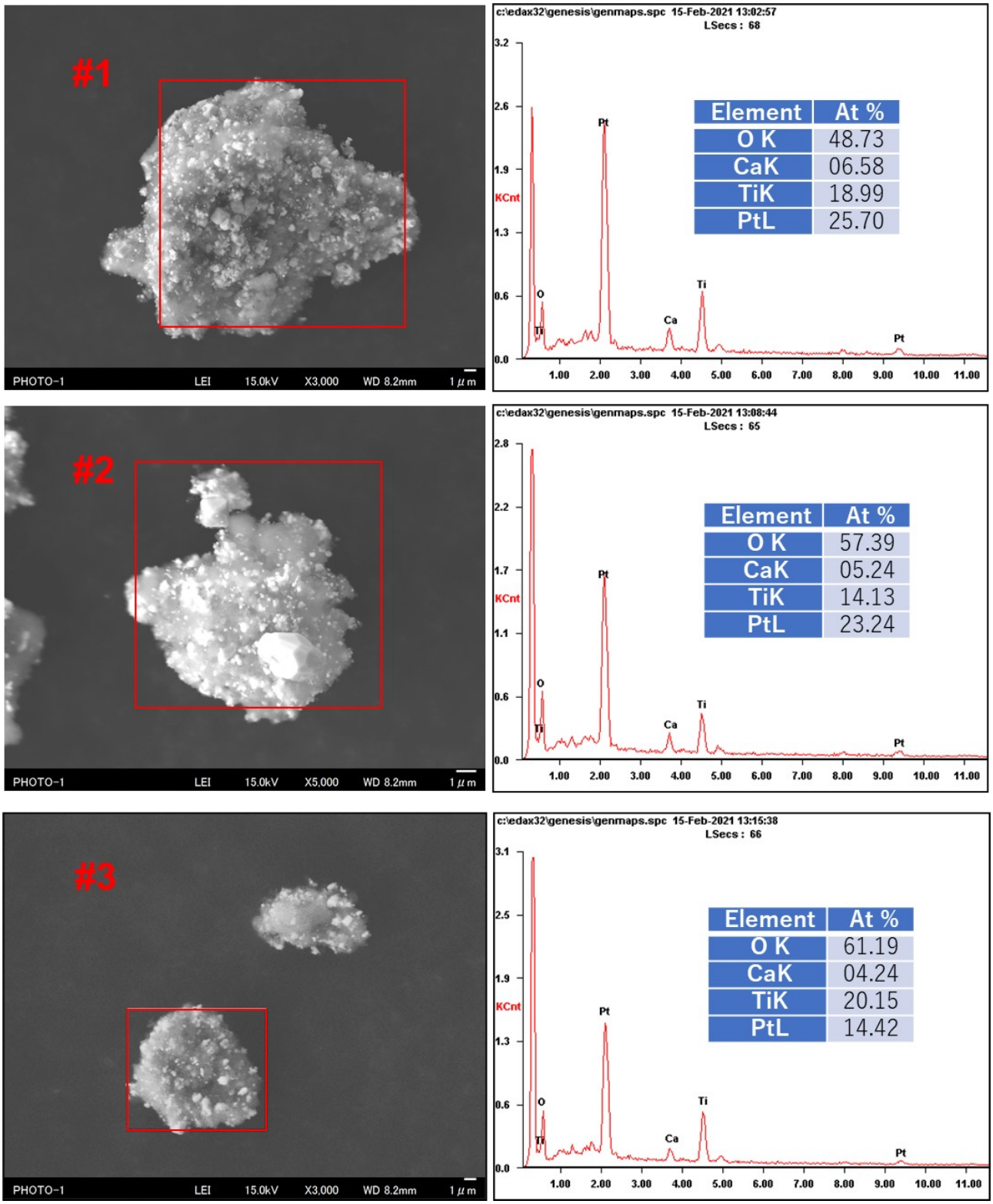

Fig. S5 SEM-EDX of $CaPt_2/TiO_x$ at different positions of #1-#3.

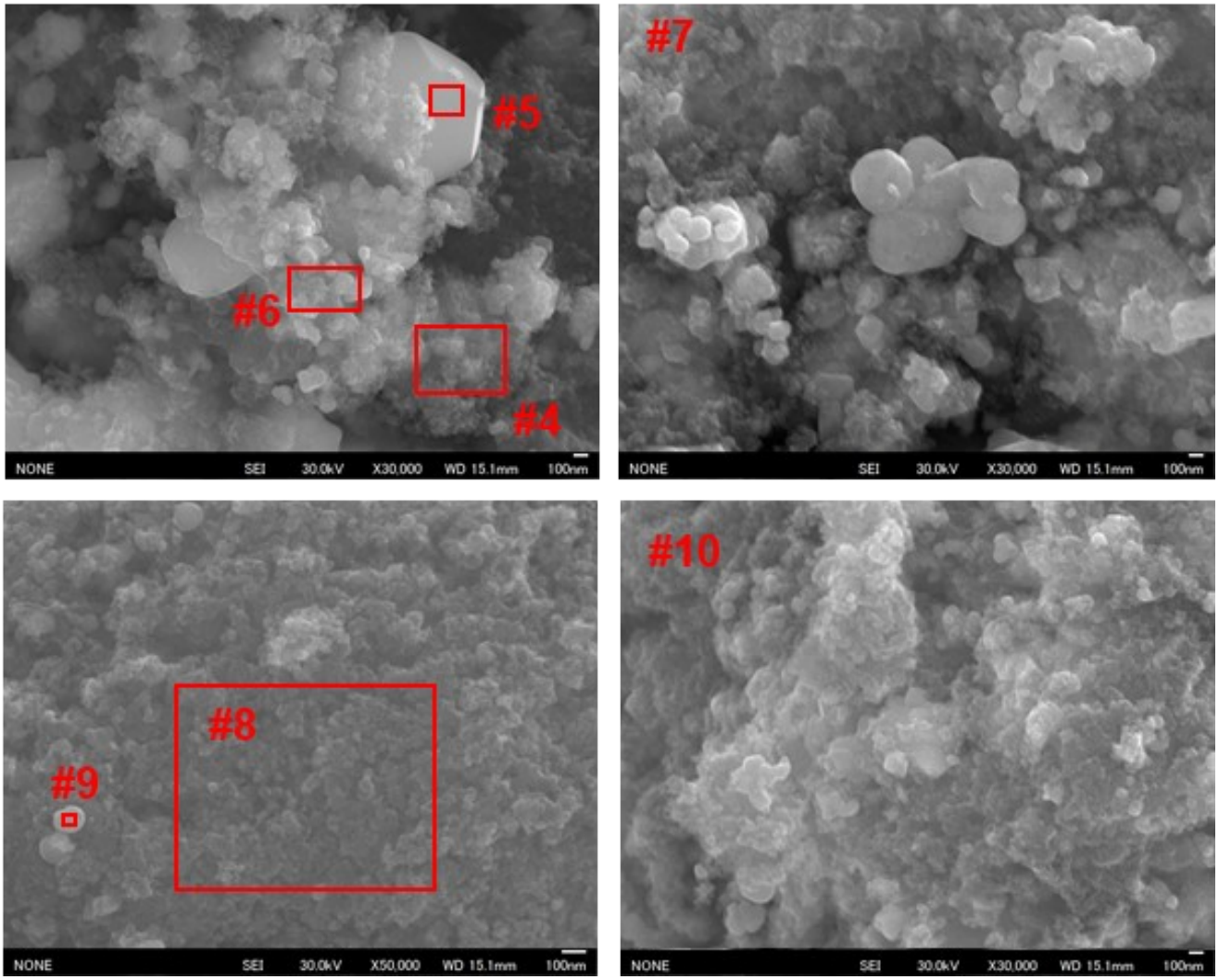

Fig. S6 SEM-EDX of $CaPt_2/TiO_x$ at different positions of #4-#10.

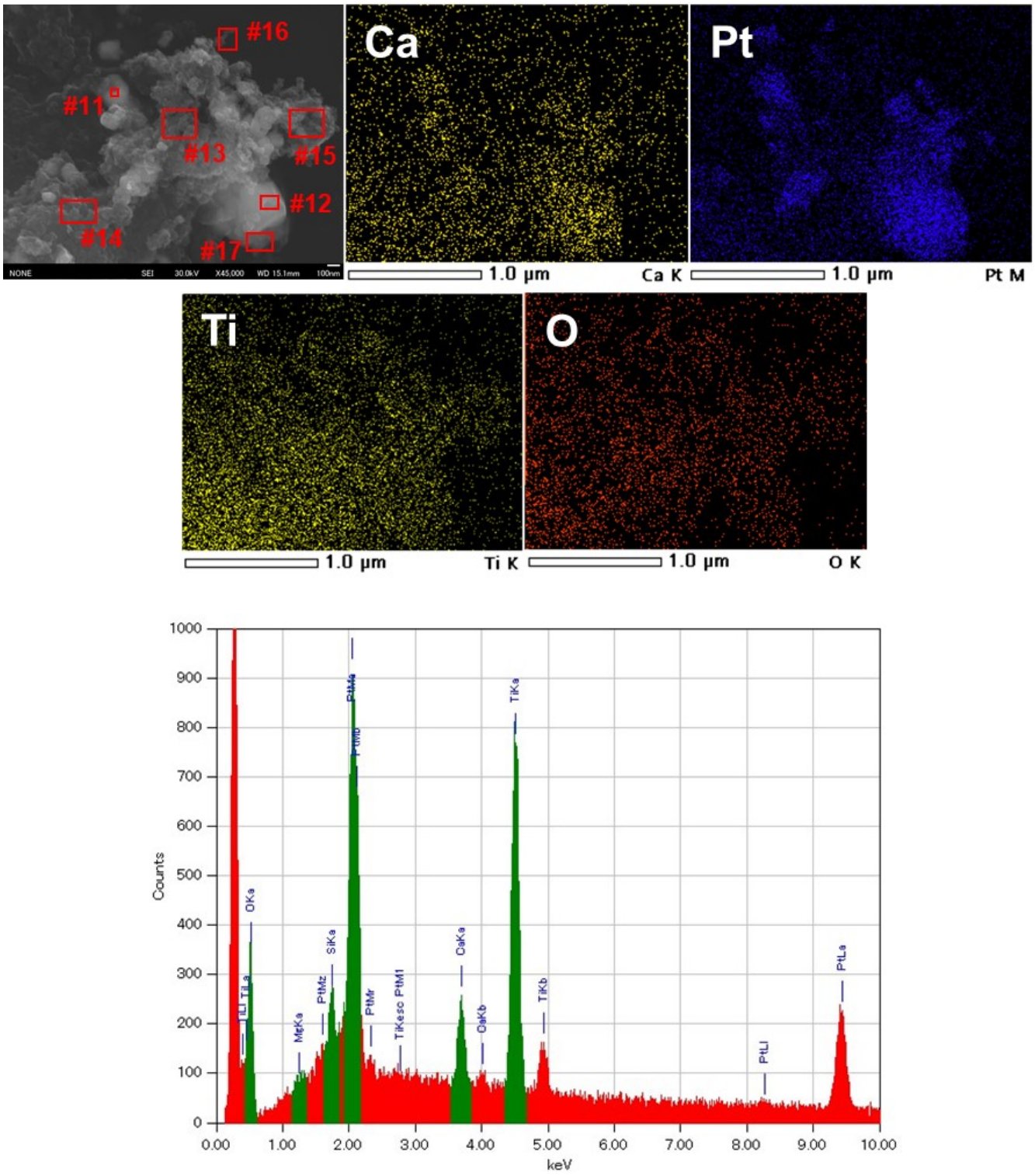

Fig. S7 SEM-EDX of $CaPt_2/TiO_x$ at different positions of #11-#17 and the elemental mappings.

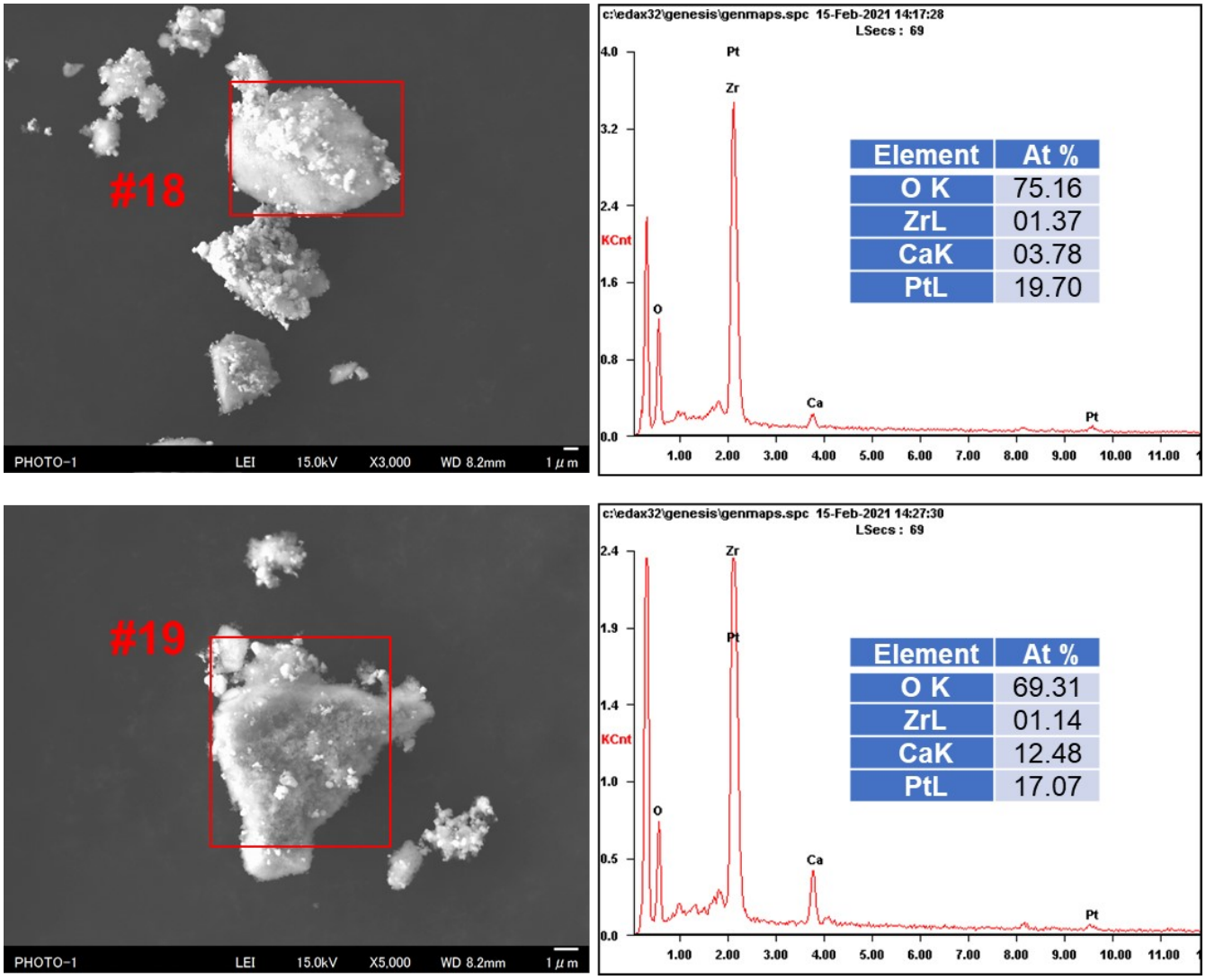

Fig. S8 SEM-EDX of $CaPt_2/ZrO_x$ at different positions of #18 and #19.

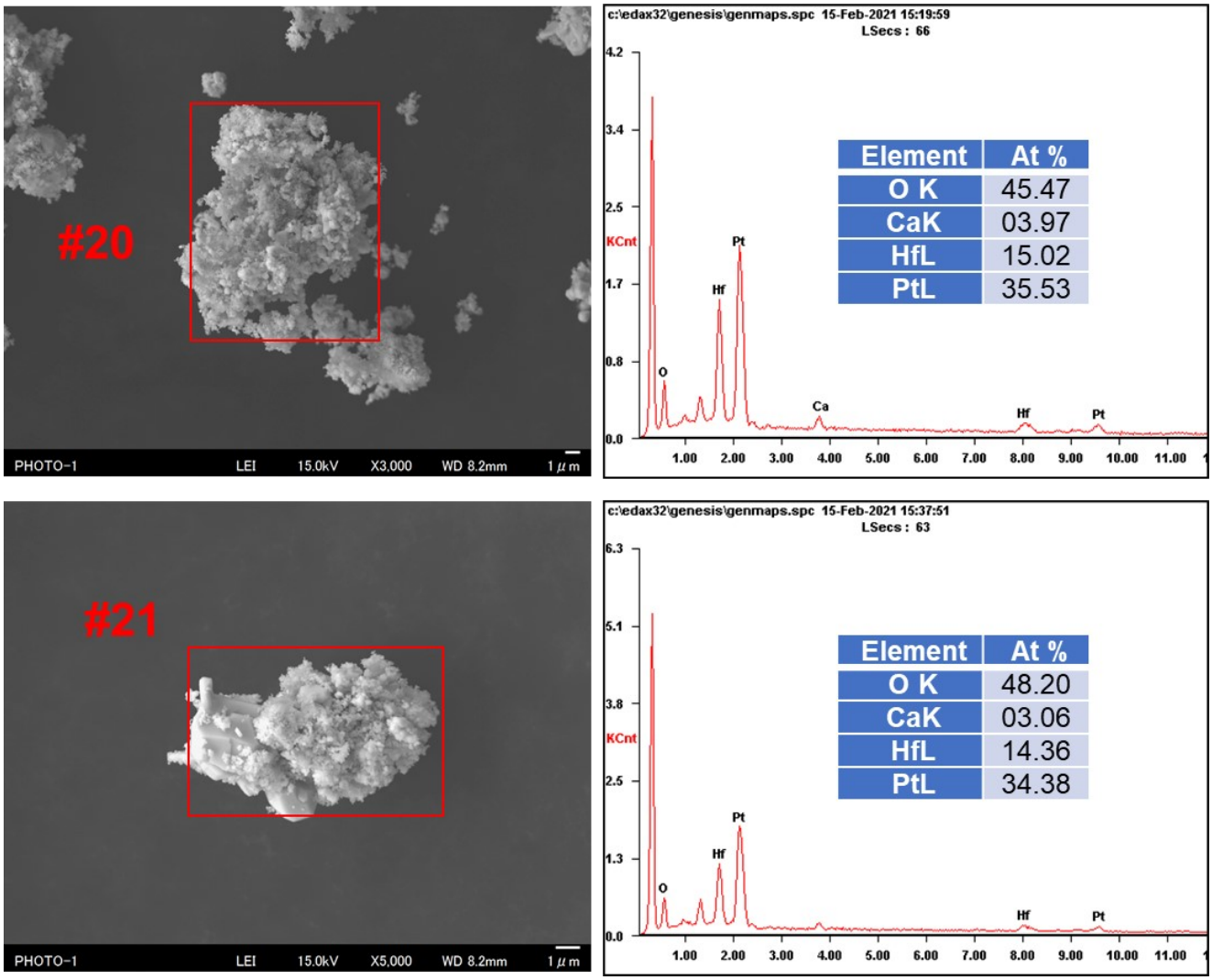

Fig. S9 SEM-EDX of $CaPt_2/HfO_x$ at different positions of #20 and #21.

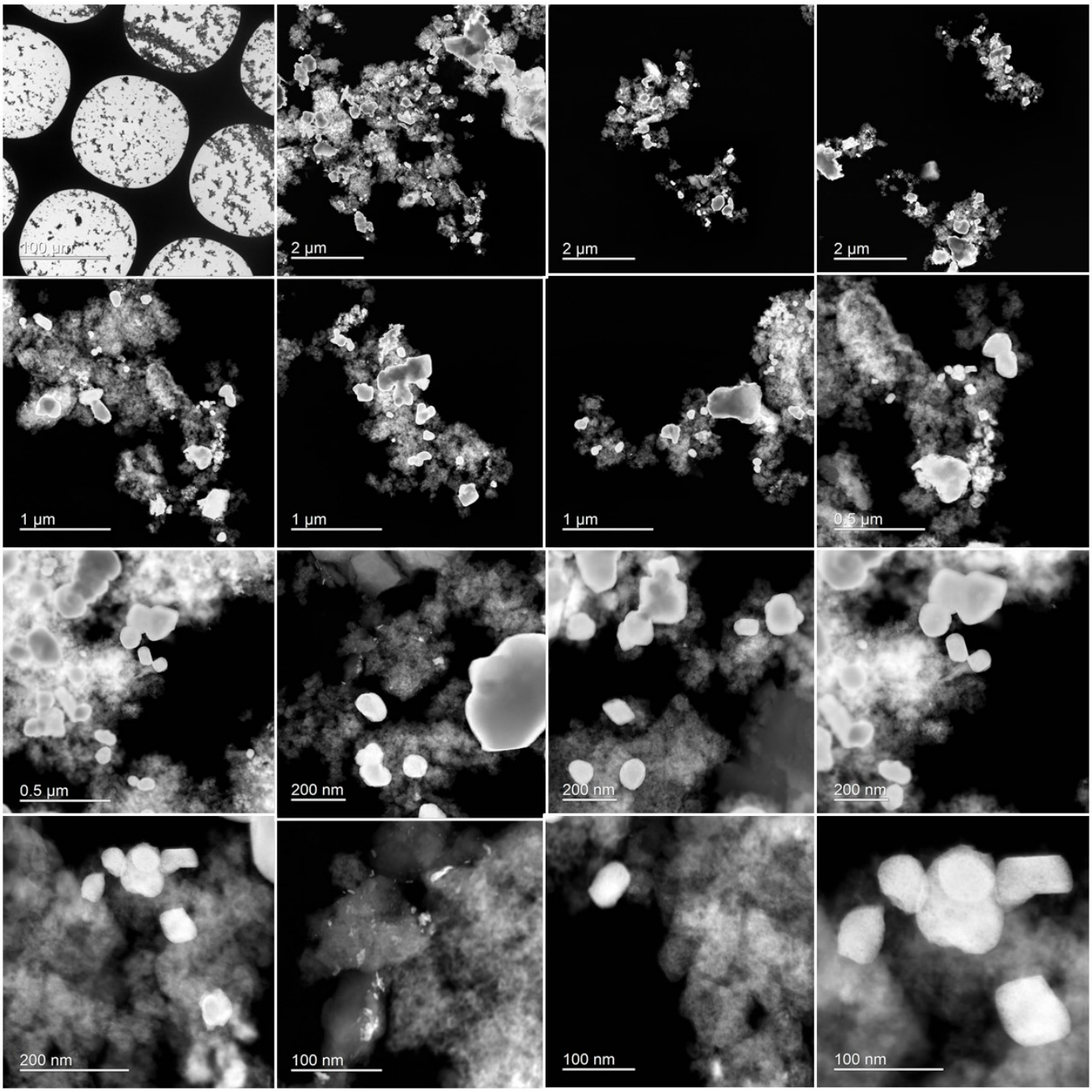

Fig. S10 TEM images of $CaPt_2/TiO_x$.

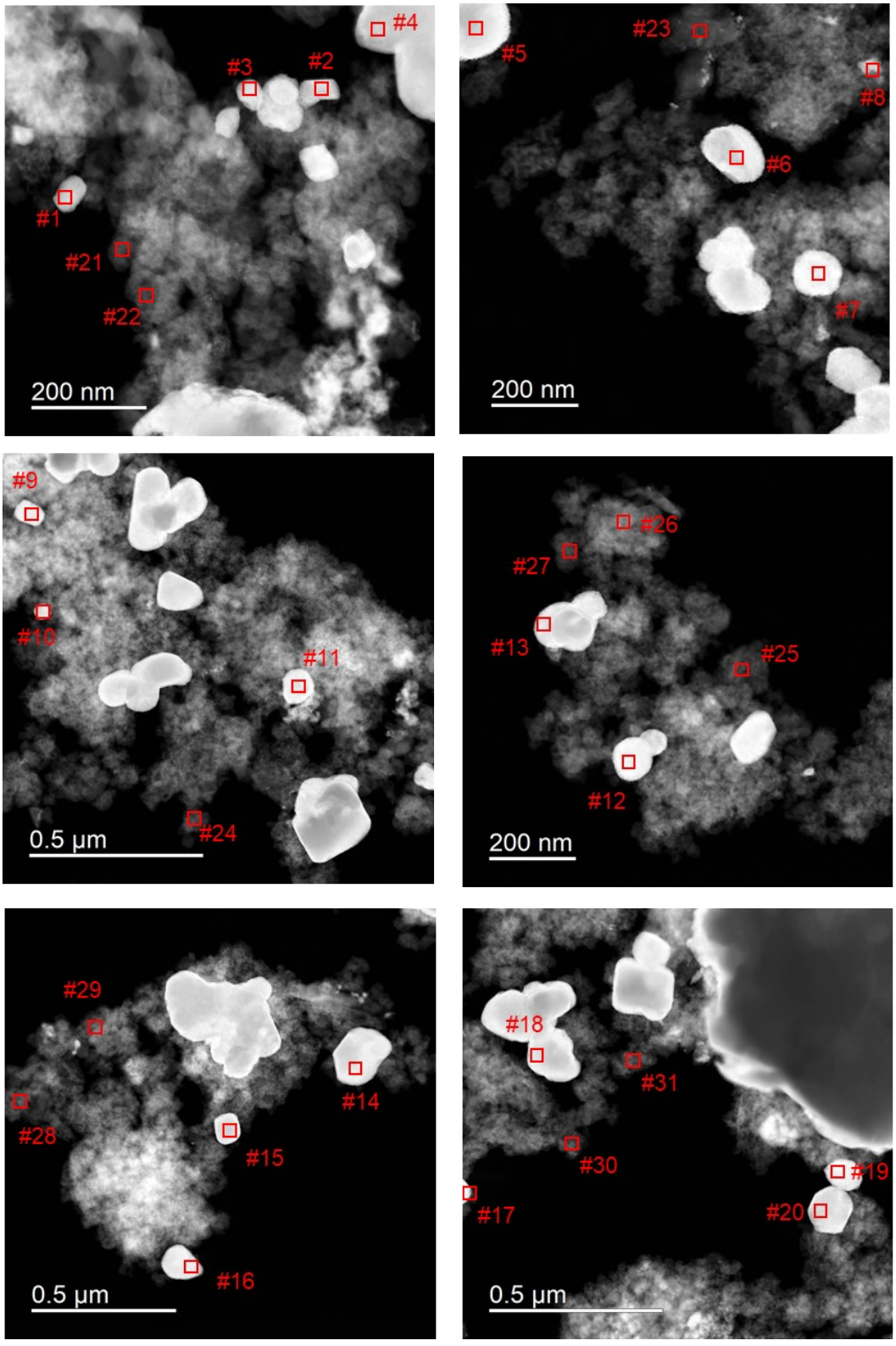

Fig. S11 TEM-EDX of $CaPt_2/TiO_x$ at different positions of #1-#31.

Table S2 Summary of the molar ratios measured by SEM-/TEM-EDX for $CaPt_2$ supported on TiO_x, ZrO_x and HfO_x.

Sample	Molar ratio of main constituent elements [mol%]						
	Measurement	Position		Ca	Pt	Ti, Zr or Hf	O
$CaPt_2/TiO_x$	SEM	1		6.6	25.7	19.0	48.7
		2		5.2	23.2	14.1	57.4
		3		4.2	14.4	20.2	61.2
		4		3.8	9.8	19.1	67.3
		5		3.9	24.8	15.2	56.2
		6		3.9	10.0	13.9	72.2
		7		7.9	21.5	15.1	55.4
		8		1.9	6.6	23.8	67.8
		9		2.3	7.2	17.8	72.7
		10		5.7	14.7	15.6	64.1
		11		4.7	10.9	7.8	76.6
		12		8.2	18.2	8.4	65.2
		13		1.3	2.9	9.4	86.4
		14		1.7	2.2	12.7	83.4
		15		1.2	3.6	10.1	85.2
		16		1.1	2.9	3.1	92.9
		17		5.7	12.9	11.4	70.1
	TEM	Pt-rich position	1	10.9	58.1	4.9	26.1
			2	15.2	71.2	3.1	10.5
			3	9.8	52.7	10.0	27.5
			4	18.7	72.2	1.9	7.3
			5	21.9	64.8	5.5	7.8
			6	23.9	66.4	1.1	8.6
			7	16.1	47.2	18.6	18.2
			8	1.4	7.6	45.4	45.6
			9	13.9	55.7	20.3	10.1
			10	11.4	59.6	22.2	6.9
			11	9.5	47.3	29.2	14.1
			12	11.6	46.8	19.3	22.4
			13	16.4	70.1	0.9	12.6
			14	13.9	64.6	14.4	7.0
			15	17.1	73.3	1.8	7.8
			16	16.5	74.0	3.5	6.1
			17	13.5	58.6	8.8	19.2
			18	19.0	70.4	3.5	7.2
			19	14.3	58.1	13.0	14.6
			20	18.8	71.5	1.4	8.3
		Ti-rich position	21	1.3	0.3	43.0	55.3
			22	1.0	0.2	45.6	53.2
			23	1.6	0.5	33.4	64.5
			24	2.7	0.4	68.6	28.3
			25	1.5	0.1	41.2	57.1
			26	2.1	0.1	39.5	58.3
			27	1.6	0.2	47.0	51.3
			28	1.8	0.4	33.1	64.8
			29	1.4	0.1	40.0	58.6
			30	1.8	0.5	43.3	54.5
			31	1.7	0.8	47.8	49.6

$CaPt_2/ZrO_x$	SEM	18	3.8	19.7	1.4	75.2
		19	12.5	17.1	1.1	69.3
$CaPt_2/HfO_x$	SEM	20	4.0	35.5	15.0	45.5
		21	3.1	34.4	14.4	48.2

Table S3 Catalytic performances of commercial Pt/C and $CaPt_2/TiO_x$ in hydrogenation of ketones to alcohols.

Catalyst	Catalyst weight [mg]	Reactant	Time [h]	Yield [a] [%]	Reaction rate [$x10^{-6}$ mol/s/g-cat]	Adsorbed amount of CO [cm^3/g-cat]	Number of active site [b] [$x10^{19}$ g-cat^{-1}]	TOF [s^{-1}]
Pt/C	3.5	cyclohexanone	4	9	2.63	1.99	5.35	0.030
		cyclohexanone	8	12	1.75			0.020
		cyclohexanone	12	16	1.56			0.018
		cyclohexanone	16	27	1.97			0.022
$CaPt_2/TiO_x$	7.5	cyclohexanone	16	6	0.20	0.02	0.06	0.190
$CaPt_2/ZrO_x$	7.5	cyclohexanone	8	6	0.40	0.31	0.84	0.029
		cyclohexanone	16	11	0.37			0.026
		cyclohexanone	24	17	0.38			0.027
		cyclohexanone	32	28	0.47			0.034
		acetophenone	16	8	0.27			0.019
$CaPt_2/HfO_x$	7.5	cyclohexanone	16	6	0.20	0.01	0.01	0.84

a) H-NMR yield using 1,3,5-trimethoxybenzene as an internal standard.

b) Calculated with an assumption that a CO molecule adsorbed on an active site.

Table S4 Comparison of TOFs obtained with Pt-based catalysts in hydrogenation of ketones to alcohols.

Catalysts	Reactant	H_2 pressure [MPa]	Temperature [℃]	TOF [s^{-1}]	ref.
Pt/C	cyclohexanone	0.1	R.T.	0.02-0.03	This work
$CaPt_2/TiO_x$	cyclohexanone	0.1	R.T.	0.19	
$CaPt_2/ZrO_x$	cyclohexanone	0.1	R.T.	0.03	
	acetophenone	0.1	R.T.	0.02	
$CaPt_2/HfO_x$	cyclohexanone	0.1	R.T.	0.84	
Pt(0) catalyst	cyclohexanone	0.6	75	0.26	[1]
Pt/MCM-41	acetophenone	0.1	R.T.	0.04-0.15	[2]
Pt-Fe nanocubes	acetophenone	0.1	70	0.29	[3]
Pt-Fe nanowires	acetophenone	0.1	70	1.63	
0.78%Pt/Al_2O_3	acetophenone	0.09	100	104000	[4]
0.95%Pt/TiO_2	acetophenone	0.09	100	63000-2400000	

References

1. M. J. Jacinto, R. Landers, and L. M. Rossi, *Catal. Comm.*, 2009, **10**, 1971.
2. Z. Wang, K.-D. Kim, C. Zhou, M. Chen, N. Maeda, Z. Liu, J. Shi, A. Baiker, M. Hunger, and J. Huang, *Catal. Sci. Technol.*, 2015, **5**, 2788.
3. W. Wu, J. Li, Z. Chen, W. Chen, H. Pang, K. Ma, and J. Zeng, *J. Catal.*, 2019, **373**, 209.
4. S. D. Lin, D. K. Sanders, and M. A. Vannice, *J. Catal.*, 1994, 147, 370.

