Electronic Supplementary Information

Novel Ca-doped $CePO_4$ Supported Ruthenium Catalyst with Superior Catalytic Performance for Aerobic Oxidation of Alcohols

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1. Experimental section

1.1 Preparation of the catalysts

The $CeCaPO_4$ and $CePO_4$ supports were prepared by the chemical precipitation method. In our experiment, an aqueous solution with pH of ~2 for calcium nitrate (0.2 M) with or without cerium(III) nitrate (0.12 M) was firstly obtained through the addition of nitric acid. Another aqueous solution of diammonium hydrogen phosphate (0.18 M) with pH of ~2 was added dropwise to the above solution with vigorous stirring. The precipitate was obtained when the pH of mixed solution was adjusted to ~10 by addition of ammonia. The suspension was kept inside a water bath at 60 ºC

and allowed to react for 24 h. The precipitate was filtrated and washed with a large amount of water, then dried at 60 ºC. The supports were obtained after the as-synthesized powders were calcinated for 2 h at 400 ºC. The Ru catalyst was prepared as follows: $CeCaPO_4$ or $CePO_4$ (1.0 g) support was added into an aqueous solution of RuCl3 (70 mL, 1.41×10^{-3} M) and vigorously stirred for 24 h at room temperature.

1.2 General procedure for the alcohol oxidation

Oxidations of alcohols were typically carried out as follows. A suspension of Ru-catalyst (0.1 g, Ru: 1 wt %) in toluene (10 mL) was stirred and then the substrate (1 mmol) was added. The resulting mixture was heated at 80 ºC under O_2 flow condition (20 mL/min). The selectivity and conversion were determined by GC analysis (Agilent 6890, equipped with an HP-FFAP capillary column and FID detector) using mesitylene as internal standard.

1.3 Oxidation of Benzyl Alcohol under Ar Atmosphere

Generally, the β-hydride elimination properties of different catalysts are investigated by the oxidation of benzyl alcohol under anaerobic conditions. In our case, the oxidation of benzyl alcohol under anaerobic condition is the integrated result of dehydrogenation and followed reoxidation of hydrido-ruthenium species due to the lattice oxygen in $RuCeCaPO_4$. The experimental details under anaerobic conditions are as follows: a suspension of the prepared Ru-based catalysts (0.1 g) in toluene (10

mL) was magnetically stirred and benzyl alcohol (1 mmol) was then added. The resulted mixture was exhausted under Ar flow (80 mL/min) for 45 min and then kept at 120 ºC for 6 h under Ar flow (40 mL/min) proceeding with the reaction of aerobic oxidation of benzyl alcohol. The selectivity and conversion were determined by GC analysis (Agilent 6890, equipped with an HP-FFAP capillary column and FID detector) using mesitylene as internal standard.

The conversion of benzyl alcohol under Ar atmosphere was confirmed to be 38% and 25% for $RuCeCaPO_4$ and $RuCePO_4$, respectively.

1.4 Recycling of $RuCeCaPO_4$ Catalyst

After reaction, the catalysts were separated by centrifugation and further washed with alcohol and deionized water respectively for three times and then dried at 60 ºC. The recovery of catalysts was investigated by using aerobic oxidation of benzyl alcohol as a model reaction.

1.5 Characterization

Characterization of catalysts

The products were analyzed by using X-ray diffractometer (X'pert Pro Super, PANAnalytical) with Cu Kα radiation (λ = 1.5418 Å), transmission electron microscope (TEM, Philips CM200), ICP-AES (Thermo IRIS Intrepid Ⅱspectrum apparatus), a UV-vis spectrometer (Cintra 20, GBC Scientific Equipment Ltd), a differential thermal and thermogravimetric apparatus (TG, SETSYS 16/18,

SETARAM), X-ray photoelectron spectrometer (XPS, PHI-5702) and O_2 pulse adsorption combined with temperature-programmed desorption and mass spectrometer (O_2 TPD-MS, AutoChemII2920, Micromeritics).

Phase analysis of the prepared samples were conducted using X-ray diffraction (XRD) with Cu Kα radiation (λ = 1.5418 Å). The diffractometer (X'pert Pro Super, PANAnalytical) was operated at a 2θ range of 10-80º with a step size of 0.02º. The morphology and grain sizes were observed through transmission electron microscopy (TEM, Philips CM200). Chemical composition of the prepared samples was separately obtained by inductively coupled plasma-atomic emission spectrometry (ICP-AES, Thermo IRIS Intrepid II spectrum apparatus).

O_2 pulse injection technology and subsequent temperature programmed desorption combined with mass spectrometric analysis (TPD-MS) were introduced to measure oxygen adsorption capacity of the catalysts and the supports. The most significant products obtained by TPD were H_2O (m/z 18), OH^- (m/z 17) and O_2 (m/z 32). The relative intensities of the corresponding peaks were presented as a function of TPD temperature.

2. Tables and Figures

Table S1. Catalytic performance of $RuCeCaPO_4$ and $RuCePO_4$ catalysts and some typical supported Ru catalysts reported in literatures for the oxidation of benzyl alcohol to benzyaldehyde with molecular oxygen under mild reaction conditions

Catalyst	T (K)	P_{O2} (bar)	Solvent	Conversion (%)	Selectivity (%)	TOF (h^{-1})	Ref.
$RuCeCaPO_4$	353	1	$PhCH_3$	100	100	408	This work
$RuCePO_4$	353	1	$PhCH_3$	100	100	148	This work
Ru/$Ni(OH)_2$ composite	363	1	$PhCH_3$	>99	99	132	[1a]
$Ru(OH)_x/TiO_2$	353	1	$PhCH_3$	>99	>99	100	[1b]
$Ru^{(III)}$/HAp	353	1	$PhCH_3$	100	>99	2	[1c]
Ru/Al_2O_3	356	1	$PhCF_3$	>99	>99	40	[1d]
RuHAp-γ-Fe_2O_3	363	1	$PhCH_3$	>99	99	196	[1e]
RuO_2/FAU zeolite	353	1	$PhCH_3$	100	>99	8.7	[1f]
Ru-Co-Al-hydrotalcite	333	1	PhCH3	100	96	9	[1g]
$Ru^{(III)}Co^{(II)}$/HAp	363	1	$PhCH_3$	100	>99	78	[1h]
$Ru^{(III)}$/HAp-benzoic acid	333	1	Mesitylene	100	>99	242	[1i]
$RuCuHPO_4$	353	1	$PhCH_3$	100	>99	21	[1j]
Ru/CaO-ZrO_2	363	1	o-xylene	100	100	224	[1k]
Ru-CHNAP-MgO	353	1	$PhCH_3$	>99	>99	6	[1l]
Ru/CNTs	358	1	$PhCH_3$	50	100	35	[1m]
RuFAp	353	1	$PhCH_3$	>99	>99	210	[1n]
RuClAp	353	1	$PhCH_3$	>99	>99	233	[1n]

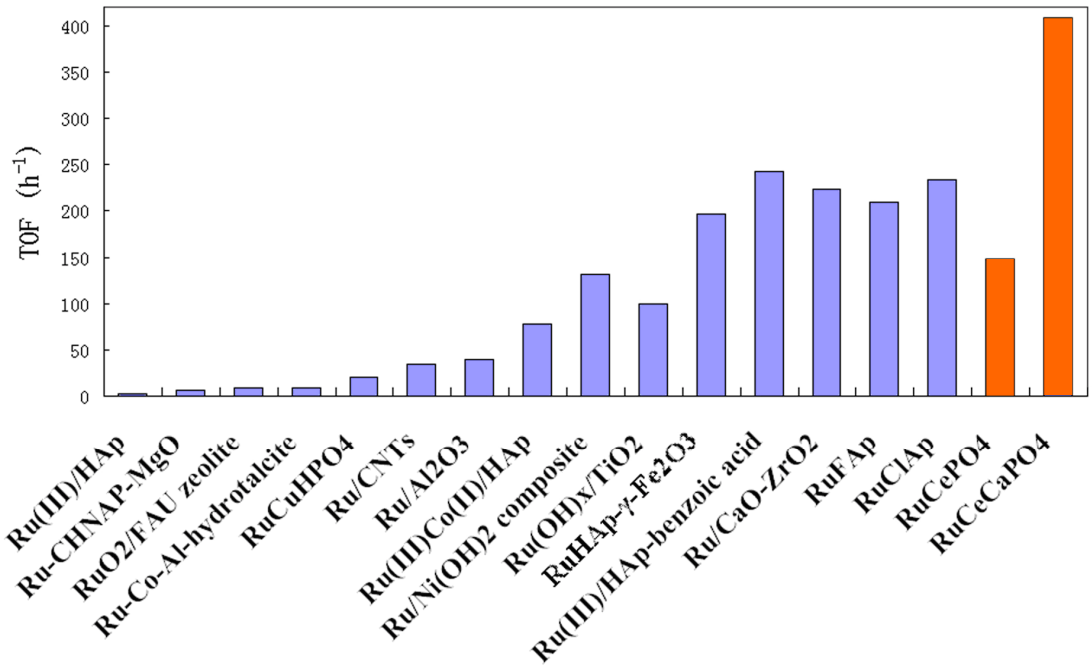
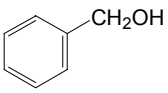
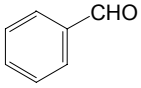
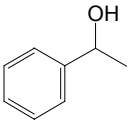
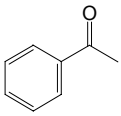
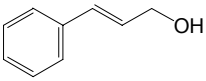
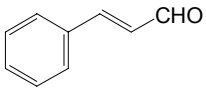
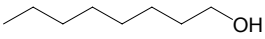
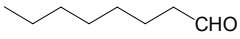
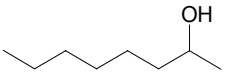
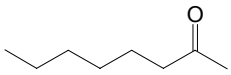

TOF (h-1)
400
350
300
250
200
150
100
50
0
Ru(III)/HAp
Ru-CHNAP-MgO
RuO2/FAU zeolite
Ru-Co-Al-hydrotalcite
RuCuHPO4
Ru/CNTs
Ru/Al2O3
Ru(III)Co(II)/HAp
Ru/Ni(OH)2 composite
Ru(OH)x/TiO2
RuHAp-γ-Fe2O3
Ru(III)/HAp-benzoic acid
Ru/CaO-ZrO2
RuFAp
RuClAp
RuCePO4
RuCeCaPO4

Table S2. Aerobic oxidation of various alcohols over $RuCeCaPO_4$ catalyst.

Entry	Alcohol	Catalyst	Time (h)	Conversion[a] (%)	Product	Selectivity (%)
1		$RuCaCePO_4$	0.25	100		100
2		$RuCePO_4$	0.67	100		100
3		$RuCaCePO_4$	1.5	96		100
4		$RuCePO_4$	4	93		100
5		$RuCaCePO_4$	2	98		100
6[b]		$RuCaCePO_4$	4	94		>99
7[b]		$RuCaCePO_4$	4	86		>99

[a] Reaction condition: 0.1 g catalyst (Ru: 1 wt %), 1mmol alcohol, 10 mL toluene, 80 °C, O_2 flow. [b] 0.2 g catalyst (Ru: 2 wt%).

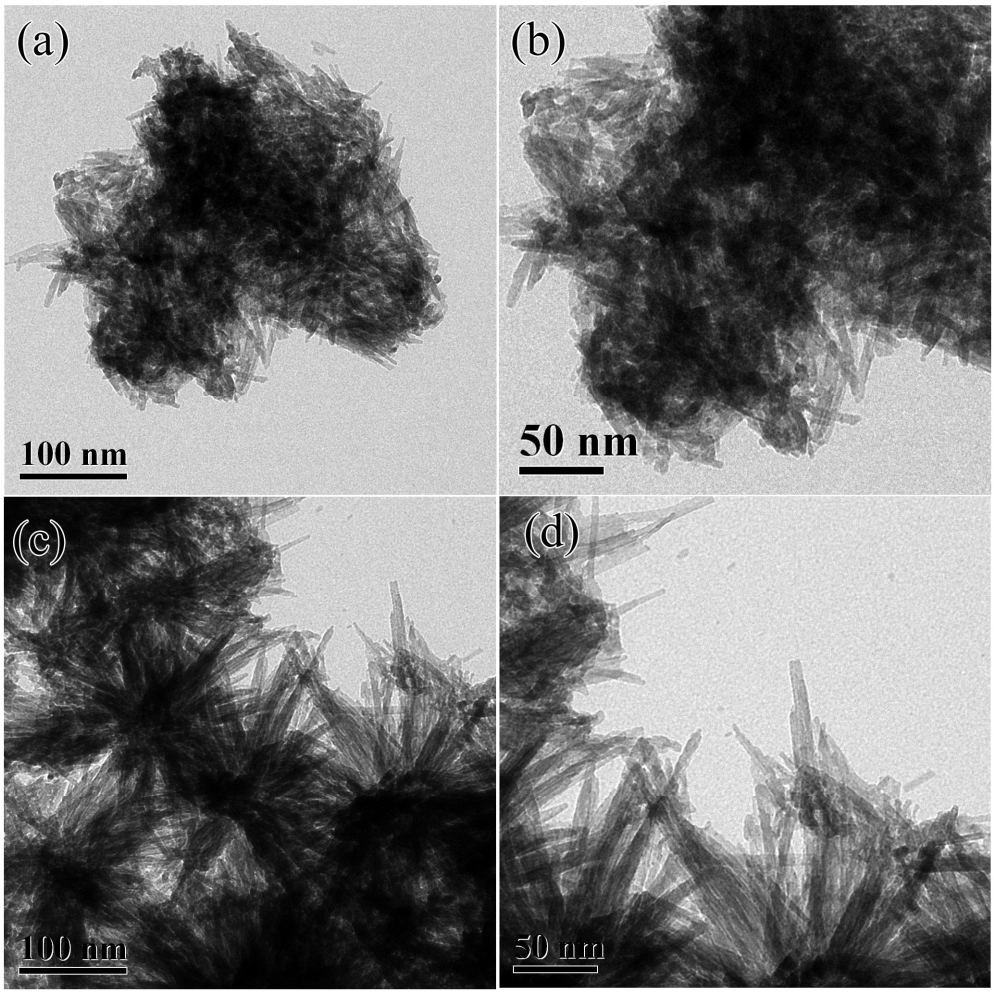


Fig. S1. TEM images of $RuCeCaPO_4$: (a), (b); $RuCePO_4$: (c), (d).

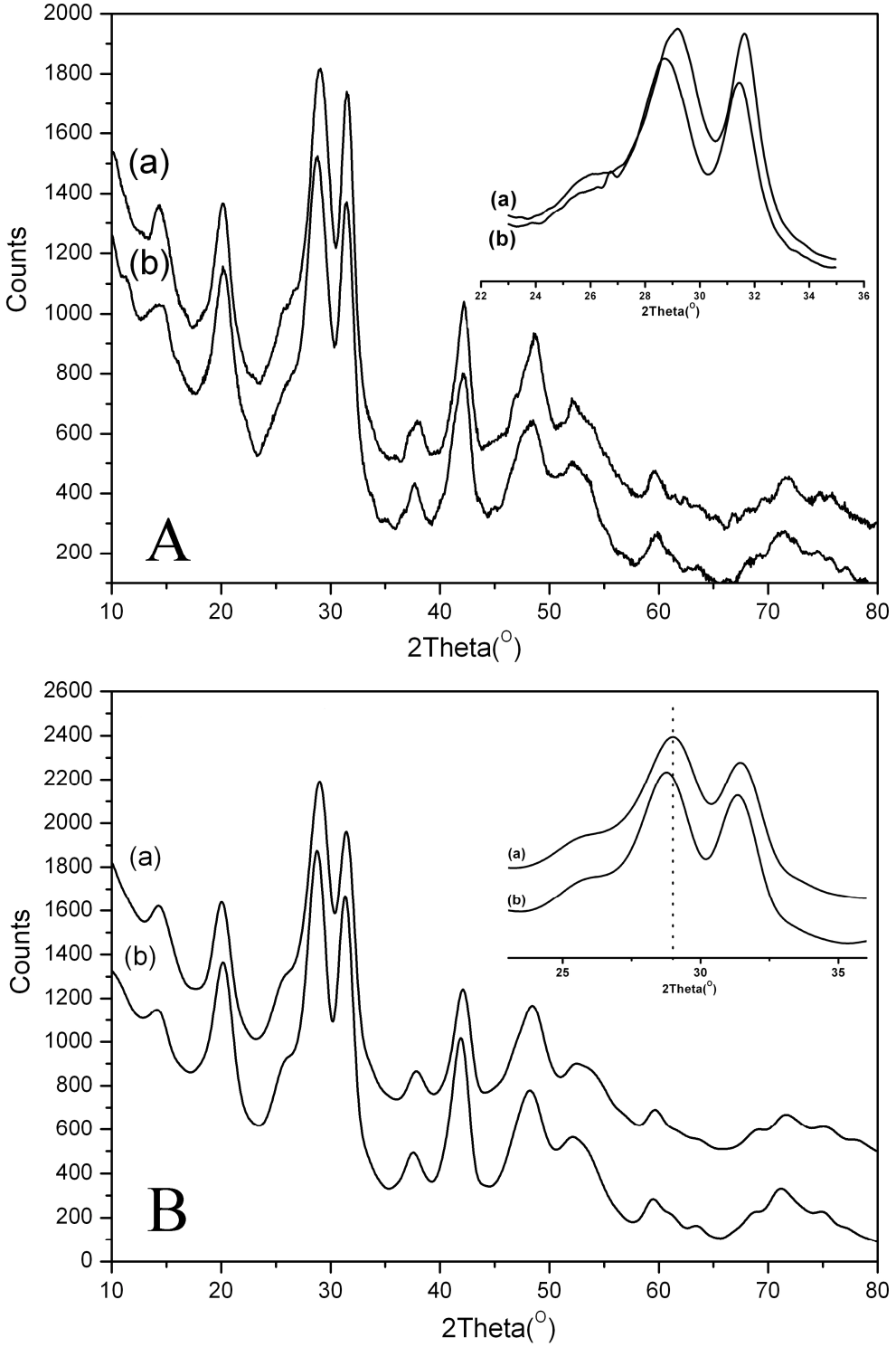


Fig. S2. The representative XRD patterns recorded for supports (A): (a) $CeCaPO_4$ and (b) $CePO_4$. Inset shows a small diffraction angle shift of $CeCaPO_4$ (0.4°); and for catalysts (B): (a) $RuCeCaPO_4$ and (b) $RuCePO_4$. Inset shows a small diffraction angle shift of $RuCeCaPO_4$ (0.4°).

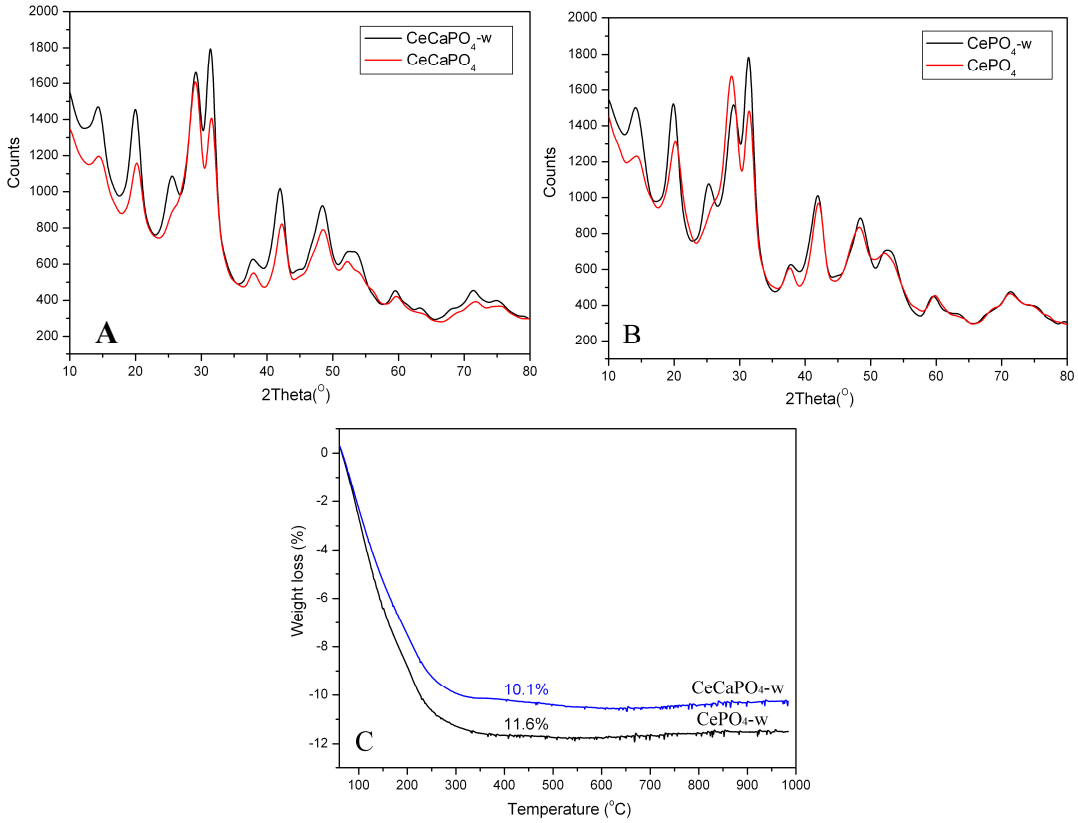


Fig. S3. XRD patterns of as-synthesized powders dried at 60 ºC, (A) $CeCaPO_4$-w, (B) $CePO_4$-w and the corresponding supports annealed at 400 ºC for 2h ($CeCaPO_4$ and $CePO_4$); (C): TG-DSC of $CeCaPO_4$-w and $CePO_4$-w.

In Fig. S3A and 3B, the XRD patterns of as-synthesized powders only dried at 60 ºC (denoted as $CeCaPO_4$-w and $CePO_4$-w) are ascribed to Rhabdophane $CePO_4 \cdot H_2O$ (JCPDS 35-614). The thermogravimetric analysis (Figure S3C) showed that $CeCaPO_4$-w and $CePO_4$-w dehydrated during heat-treatment process.

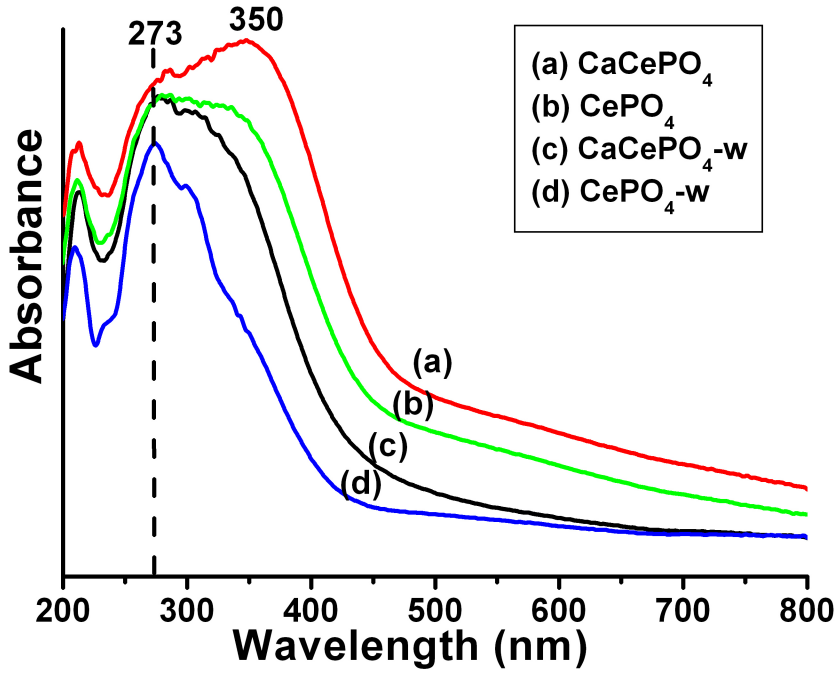


Fig. S4. UV-vis absorption spectra of $CeCaPO_4$ (a), $CePO_4$ (b), $CeCaPO_4$-w (c) and $CePO_4$-w (d).

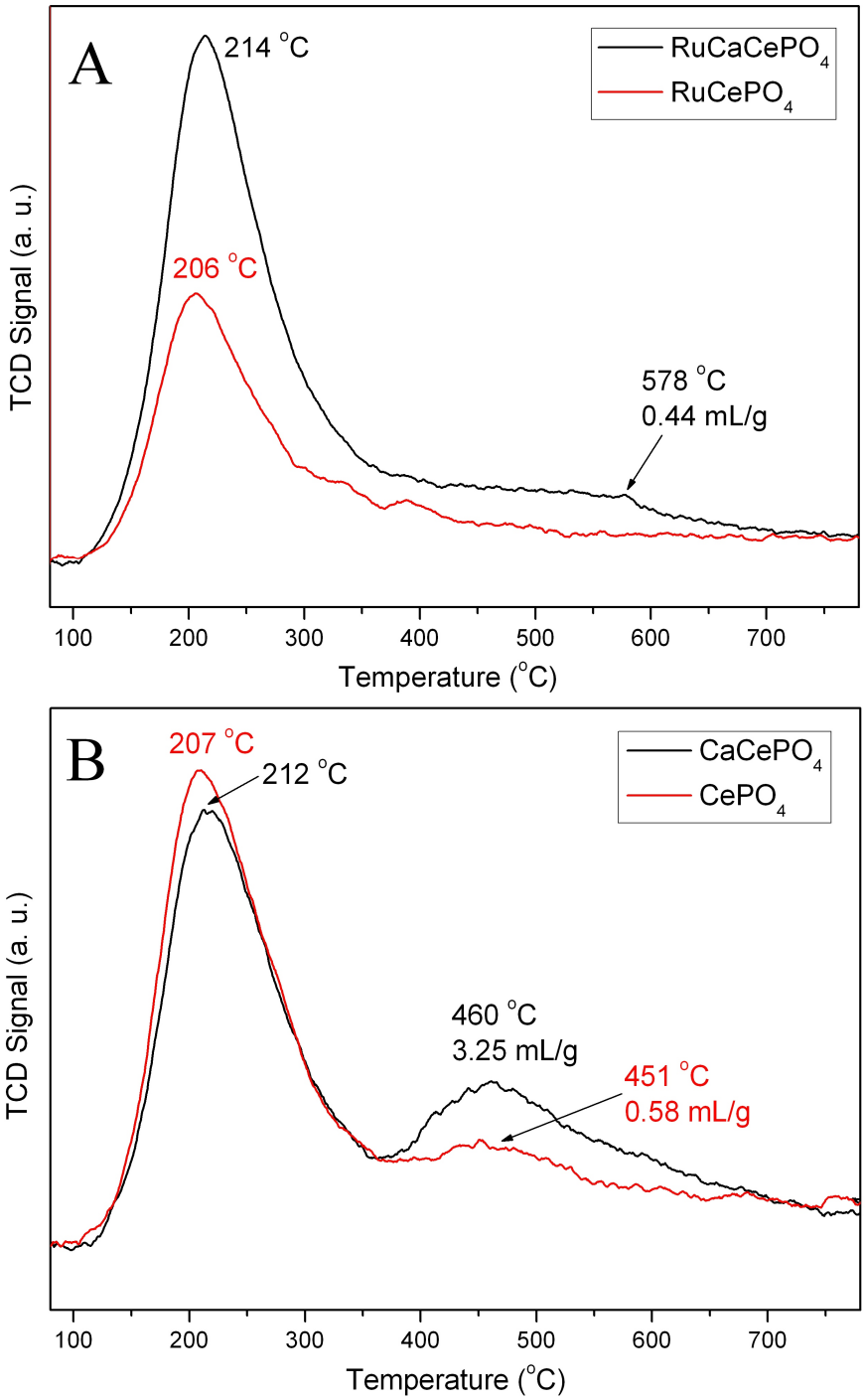


Fig. S5. O_2-TPD curve after O_2 pulse injection technology for various samples: $RuCeCaPO_4$, $RuCePO_4$, $CeCaPO_4$ and $CePO_4$.

The peaks at 206-214 °C were ascribed to desorption of H_2O at the surface of all samples based on the characterization of mass spectroscopy (Fig. S5). The amounts of desorbed O_2 decreased from 3.25 mL/g to 0.44 mL/g during Ru-exchanged process for $CeCaPO_4$, accompanied with the increase of desorption temperature of O_2.

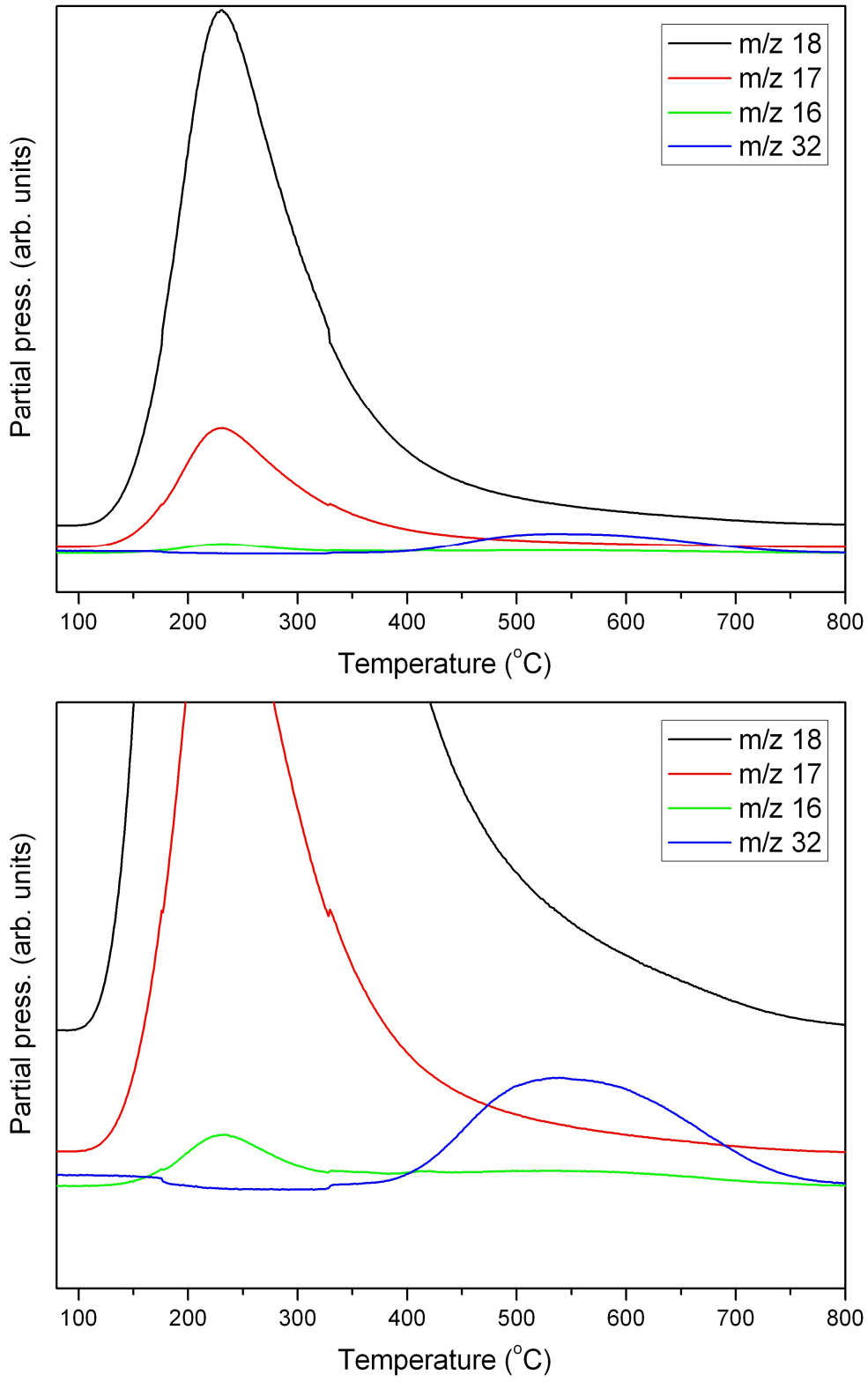


Fig. S6A. O_2 TPD-MS profiles of $RuCeCaPO_4$ catalyst after O_2 pulse injection technology

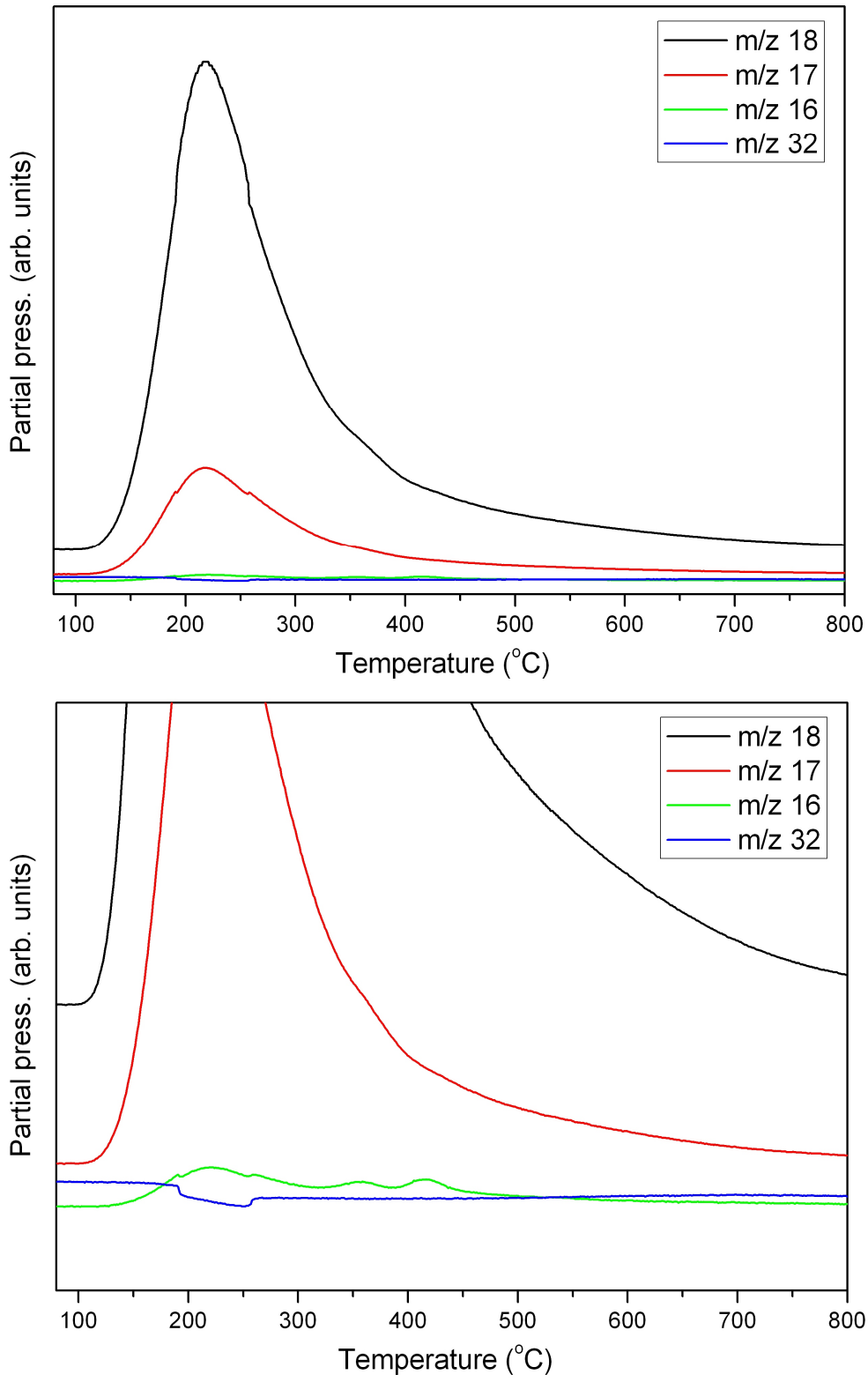


Fig. S6B. O_2 TPD-MS profiles of $RuCePO_4$ catalyst after O_2 pulse injection technology

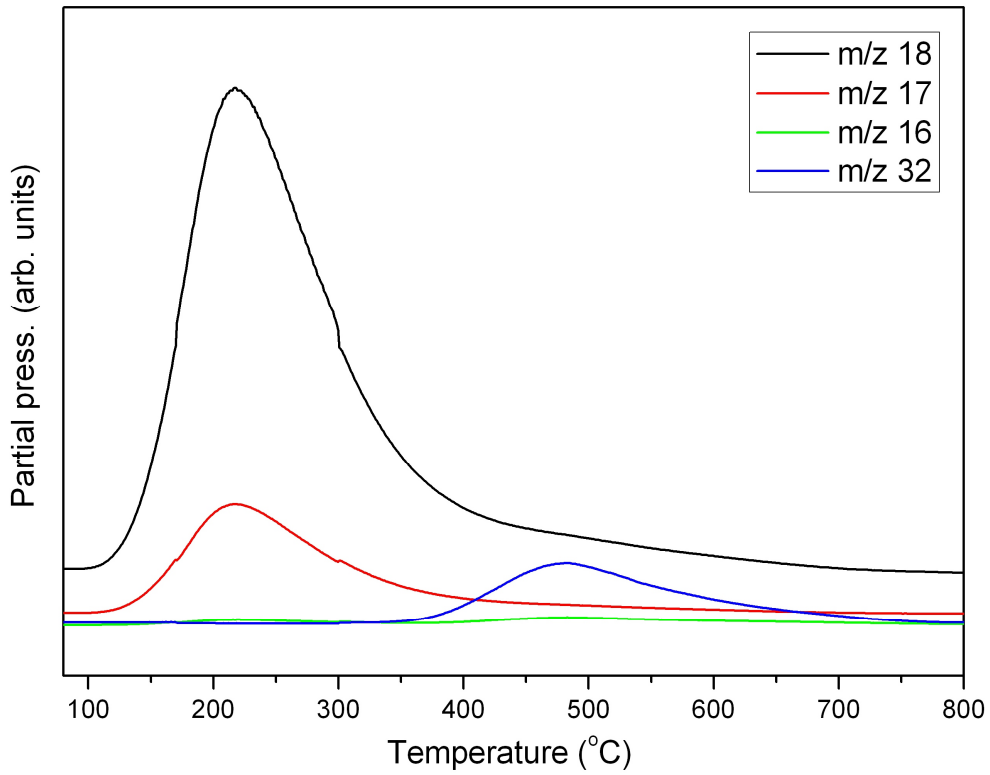


Fig. S6C. O_2 TPD-MS profiles of support ($CeCaPO_4$) after O_2 pulse injection technology

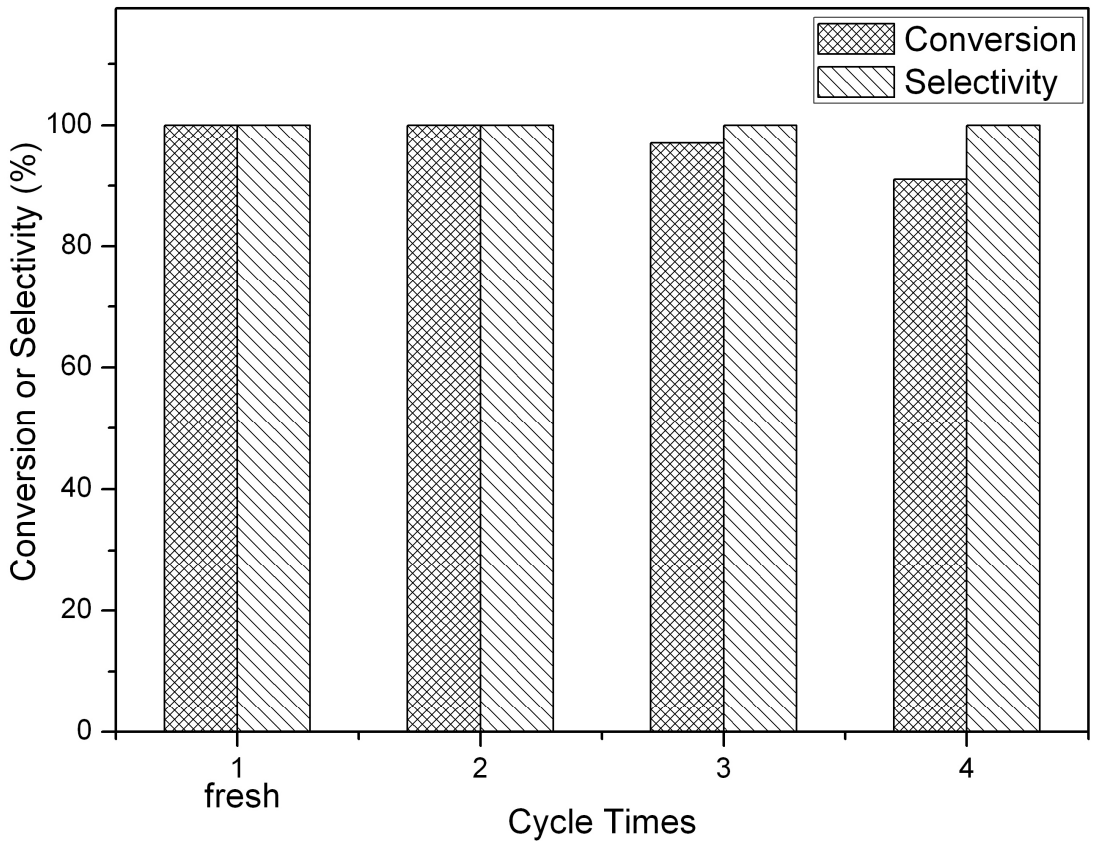


Fig. S7. Reusability of $RuCeCaPO_4$ catalyst for aerobic oxidation of benzyl alcohol. Reaction conditions: 0.1 g catalyst, 1 mmol benzyl alcohol, 10 mL toluene, O_2 flow rate, 20 mL/min; temperature, 353K; time, 15 min.

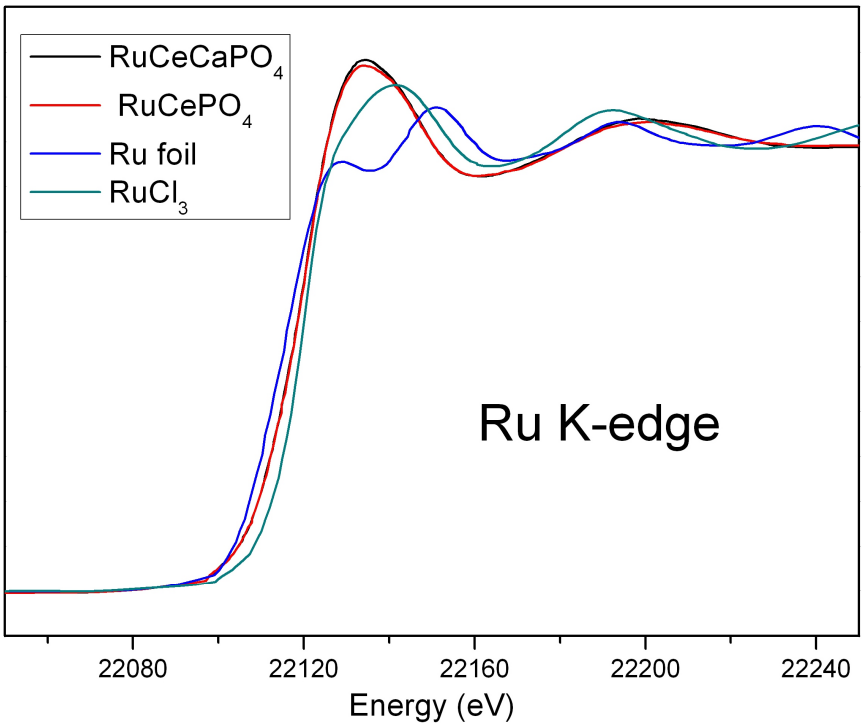


Fig. S8A. X-ray absorption near-edge fine structure spectra of $RuCeCaPO_4$, $RuCePO_4$, $RuCl_3 \cdot 3H_2O$ and Ru foil. The E_0 energy of Ru K-edge for Ru foil, $RuCeCaPO_4$, $RuCePO_4$ and $RuCl_3 \cdot 3H_2O$ are 22117, 22121, 22121, and 22121 eV, respectively. Evidently, it could be concluded that Ru^{3+} species existed in the prepared catalysts.

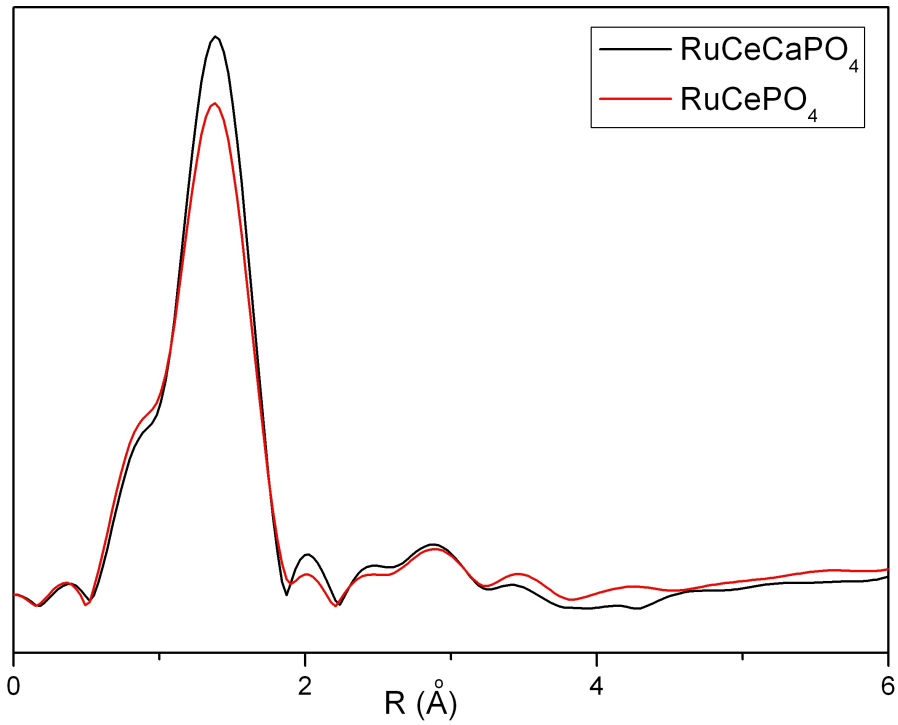


Fig. S8B. Fourier-transformed EXAFS data (k^2-weighted $\chi(k)$-function, 2.0-11.0 $Å^{-1}$) of $RuCaCePO_4$ and $RuCePO_4$. The spectra of $RuCeCaPO_4$ and $RuCePO_4$ exhibited no significant difference between their K-edge energies. Their near-edge features were identical, which indicated the similar short-range structures.

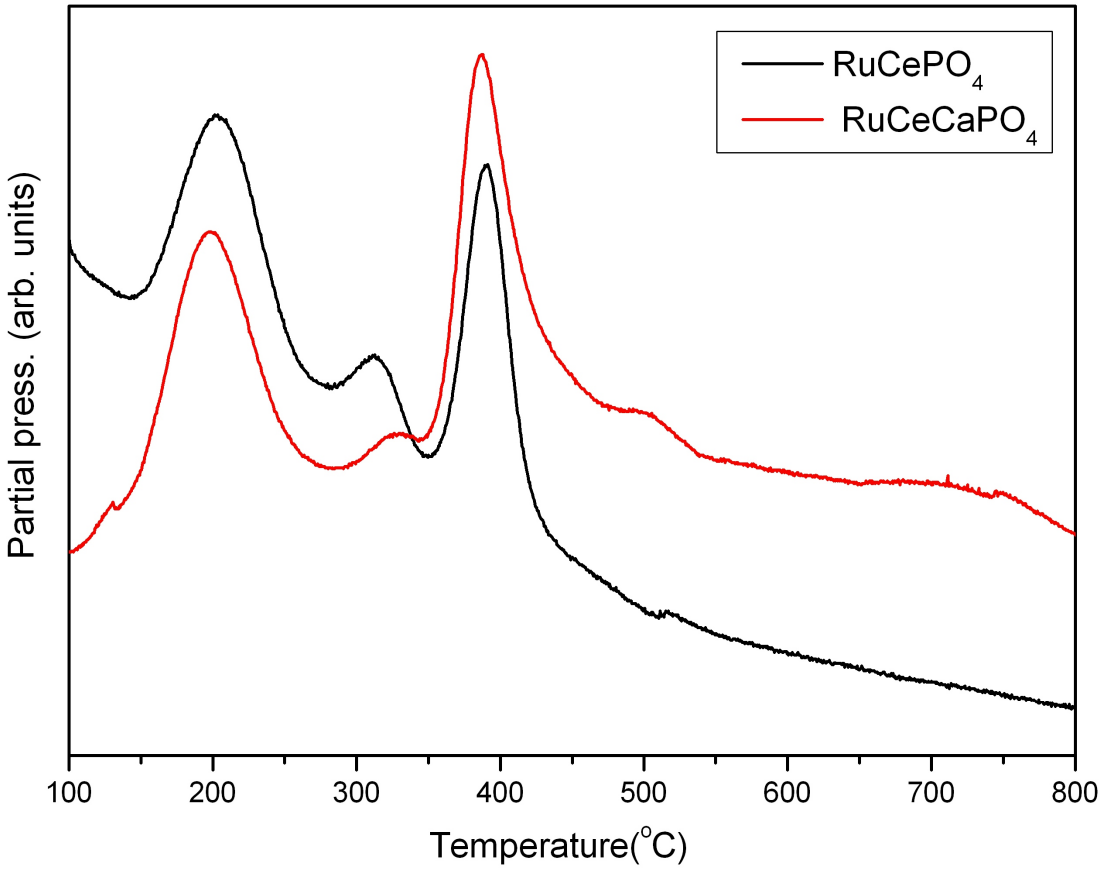
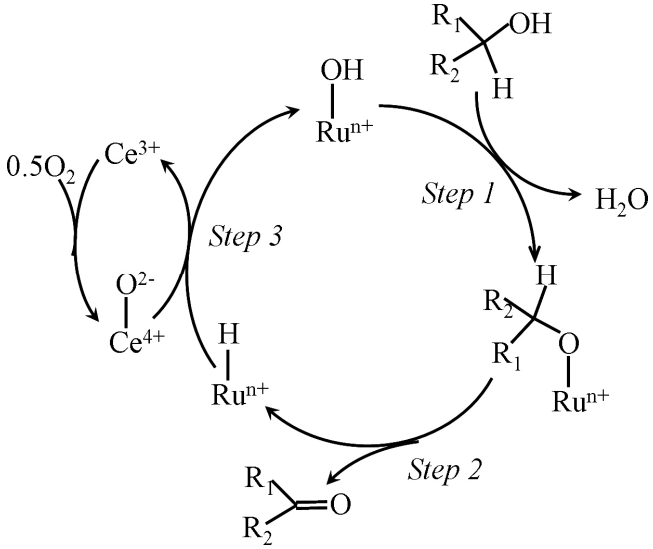


Fig. S9. CO_2 TPD-MS profiles of catalysts ($RuCeCaPO_4$ and $RuCePO_4$)



Scheme S1 Suggested reaction mechanism of aerobic oxidation of alcohols over $RuCeCaPO_4$ catalyst.