Supporting Materials

Selectively creating oxygen vacancies on $PrCe/SiO_2$ catalysts for the transformation of furfural–acetone adduct into a functionalized 1,3-diene

Yanlong Qi [a], Shijun Liu [a,b], Zaizhi Liu [c], Long Cui [a], Lingyun Huang [a,b], Yinxin Yang [a,b], Ruiyao Wu [a,b], Quanquan Dai [a], Jianyun He [a], Wei Dong [a], Chenxi Bai [a,b]*

[a] Key Laboratory of High–Performance Synthetic Rubber and Its Composite Materials, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Renmin Road, Changchun 130022, China;

[b] Applied Chemistry, University of Science and Technology of China, Jinzhai Road, Hefei 230026, China.

[c] College of Life Sciences, Jiangxi Normal University, Ziyang Road, Nanchang 330022, China

* Corresponding author: baicx@ciac.ac.cn

Table S1 Catalytic results over various catalysts.

Smaple	FAH concentration (%)	Conversion (%)	Selectivity (%)	Formation rate ($mmol/(g_{cat}\ h)$)
SiO_2	2	97	41	0.35
Ce/SiO_2	2	100	92	0.81
Ce/SiO_2	4	100	80	1.50
Ce/SiO_2	5.3	100	59	1.51
$AgCe/SiO_2$	2	100	40	0.35
$LaCe/SiO_2$	2	100	75	0.61
$PrCe/SiO_2$	2	100	96	0.83

Catalyst weight: 0.40 g; temperature: 300 °C; feed rate: 0.05 mL/min; N_2 flow rate: 50 mL/min; the result data are averaged within 1 h.

Table S2 Content of CeO_2 in $PrCe/SiO_2$ catalysts

Smaple	CeO_2 loading wt%
Ce/SiO_2	12.45
$PrCe_{0.42}/SiO_2$	11.58
$PrCe_{0.73}/SiO_2$	11.22
$PrCe_{1.07/}SiO_2$	10.87
$PrCe_{1.54}/SiO_2$	10.39
$PrCe_{2.11}/SiO_2$	9.68

$PrCe_{2.82}/SiO_2$	9.06

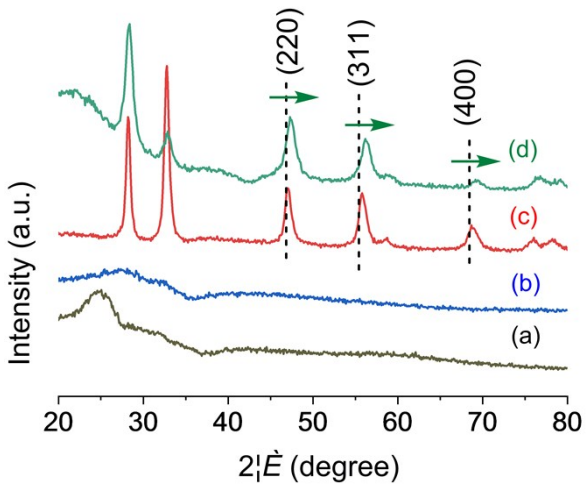

Fig.S1 XRD pattern: (a) 12wt% of Pr/SiO_2, (b) 28wt% of Pr/SiO_2, (c) Pr_6O_{11} and (d) CeO_2

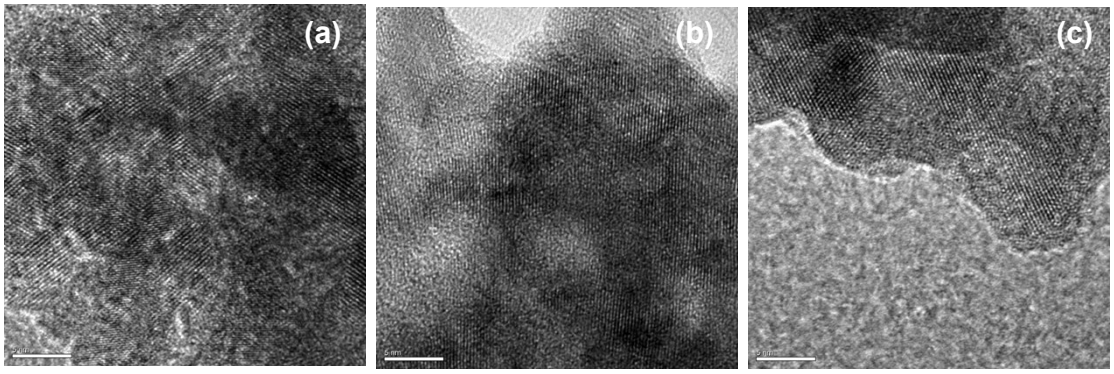

Fig.S2 HRTEM of $PrCe_{1.54}/SiO_2$ (a), $PrCe_{2.11}/SiO_2$ (b) and $PrCe_{2.82}/SiO_2$(c)

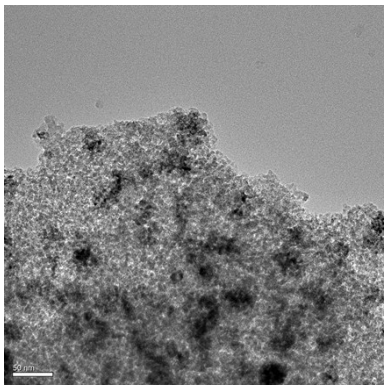

Fig. S3 TEM image of CeO_2/SiO_2

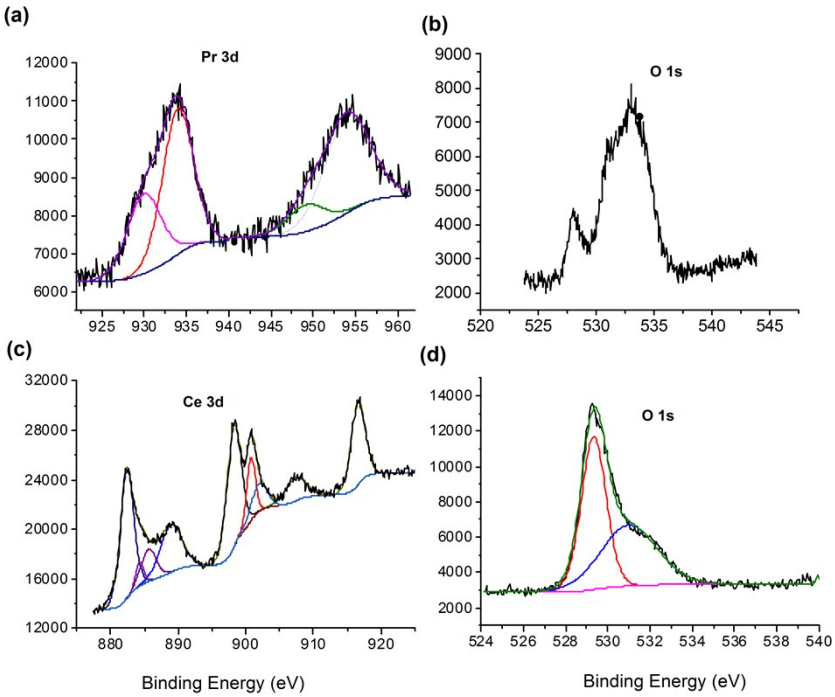

Fig. S4 XPS spectrum of pure PrO_x: (a), (b) and CeO_2: (c), (d).

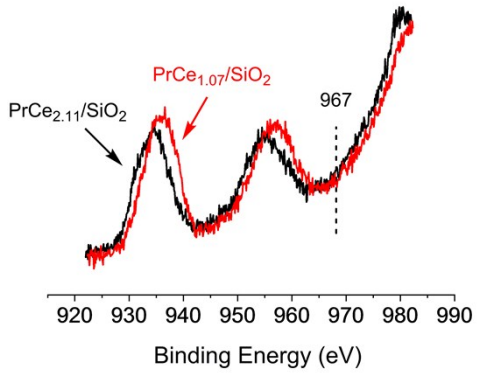

Fig.S5 XPS of Pr 3d

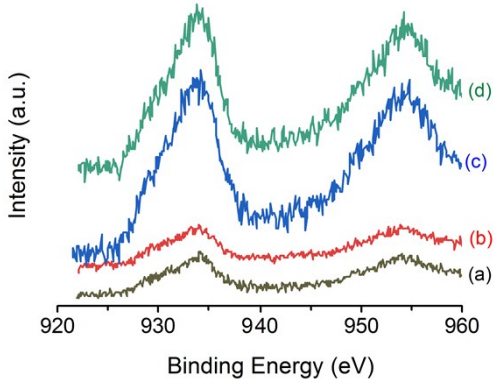

Fig. S6 XPS of Pr 3d: (a) $PrCe_{1.07}/SiO_2$, (b) $PrCe_{2.11}/SiO_2$, (c) $PrCe_{2.82}/SiO_2$, (d) Pr/SiO_2 with 28wt% of PrO_2 loading

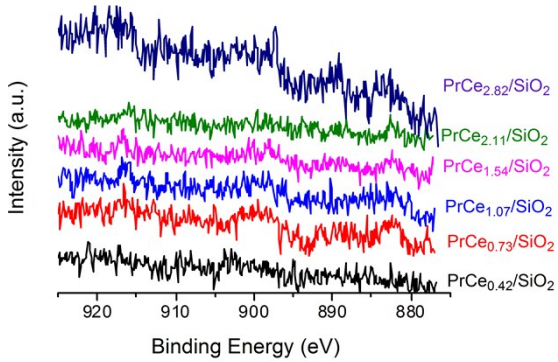

Fig. S7 XPS of Ce 3d

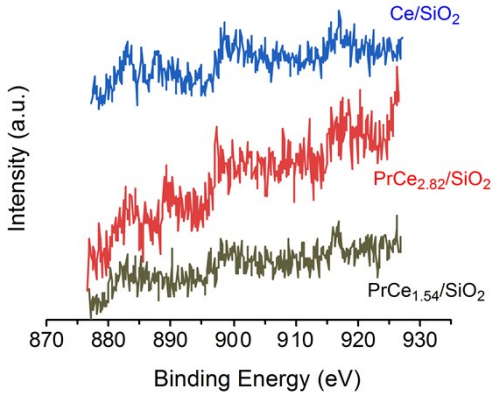

Fig. S8 XPS of Ce 3d: CeO_2/SiO_2 with 12.45 wt% of CeO_2 loading, $PrCe_{2.82}/SiO_2$ with 10 wt% of CeO_2 loading, and $PrCe_{1.54}/SiO_2$ with 9 wt% of CeO_2 loading.

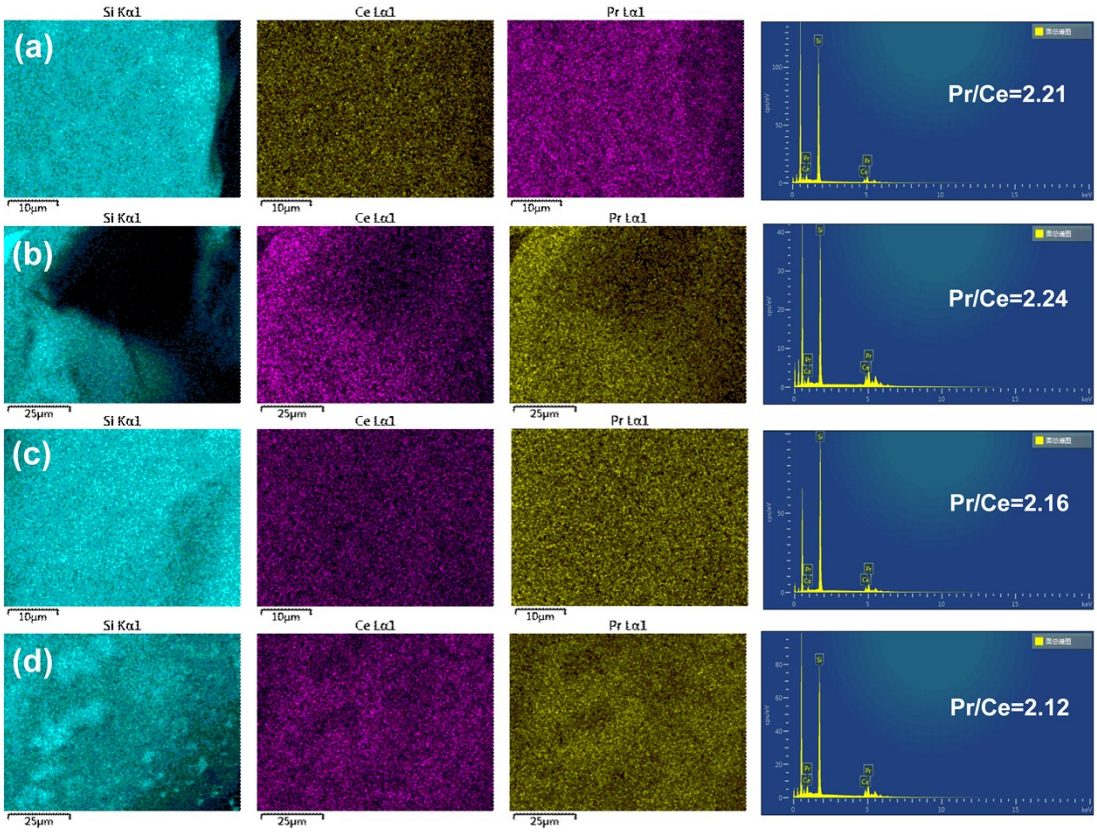

Fig. S9 SEM–EDS analysis of $PrCe_{2.11}/SiO_2$: Elemental distribution and content.

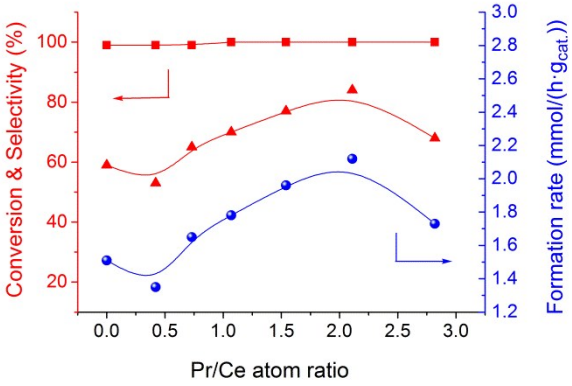

Fig. S10 Conversion, selectivity and formation rate as function of Pr/Ce atom ratio (5.3 wt% of FAH)

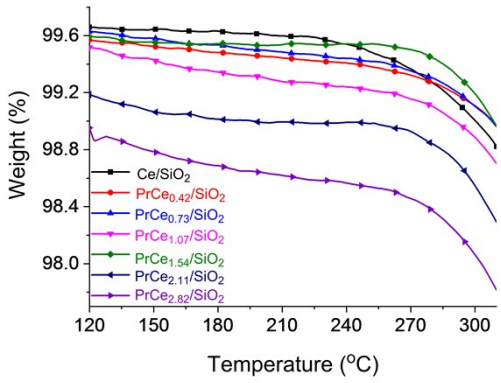

Fig. S11 TGA of spent $PrCe/SiO_2$ catalysts

Table S3 Relative concentration of oxygen vacancies

Smaple	$S_{OV}/(S_{OV}+S_{F2g})$
$PrCe_{0.42}/SiO_2$	23
$PrCe_{0.73}/SiO_2$	27
$PrCe_{1.07}/SiO_2$	41
$PrCe_{1.54}/SiO_2$	54
$PrCe_{2.11}/SiO_2$	63
$PrCe_{2.82}/SiO_2$	45

S_{F2g}: Peak area of the F2g mode at approx. 452 cm^{-1}

S_{OV}: Peak area of the oxygen vacancy at approx. 567 cm^{-1}

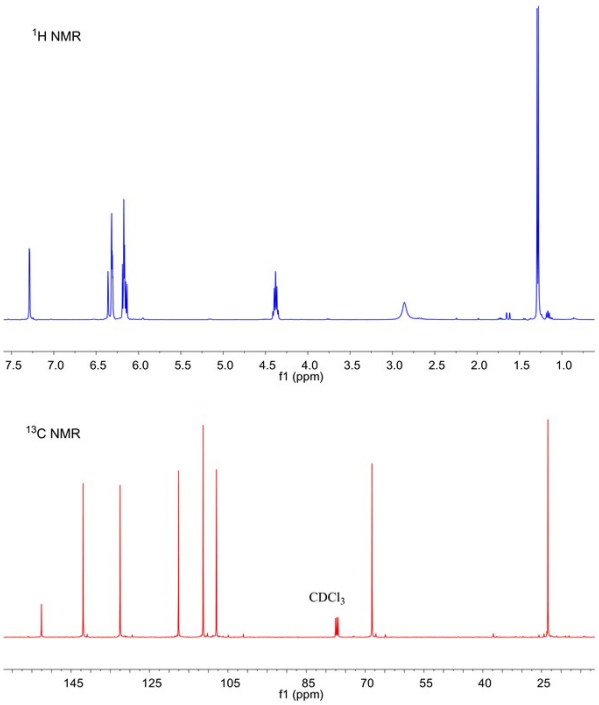

Fig.S12 ^{1}H NMR and ^{13}C NMR curve of FAH in $CDCl_3$

^{1}H NMR ($CDCl_3$ 400 MHz, ppm): δ = 1.29 (d, 3H), 2.86 (s, 1H), 4.38 (m, 1H), 6.10-6.22 (m, 2H), 6.26-6.39 (m, 2H), 7.29 (d, 1H).

^{13}C NMR ($CDCl_3$ 100 MHz, ppm): δ = 23.40, 68.25, 107.92, 111.33, 117.61, 132.49, 141.93, 152.56

Ref: *Org. Lett.*2012, **14**, 5134-5137; *J. Org. Chem.*2010, **75**, 2981-2988; *J Mol. Catal. B: Enzym.*2016, **126**, 37-45; *J. Org. Chem*. 1987, **52**, 4855-4859

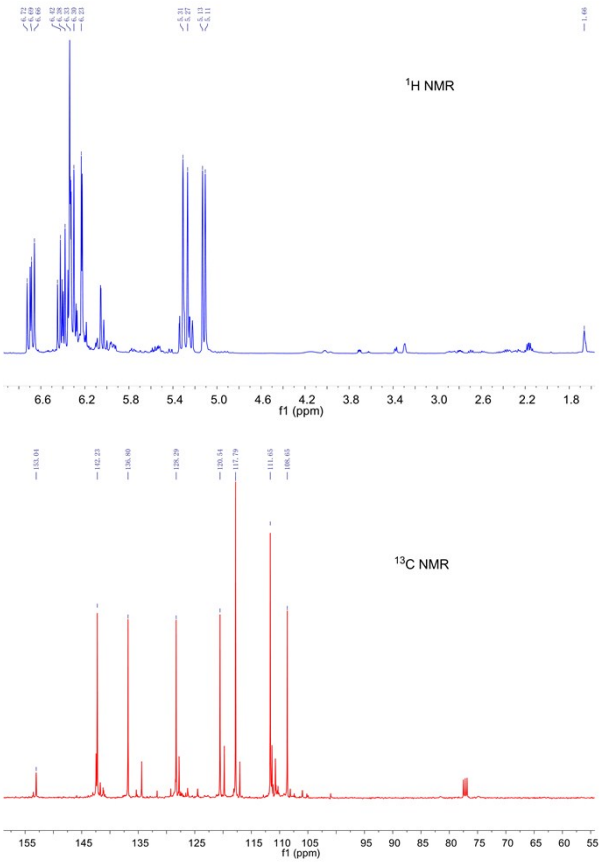

Fig.S13 ^{1}H NMR and ^{13}C NMR curve of F-diene in $CDCl_3$

^{1}H NMR ($CDCl_3$ 400 MHz, ppm): δ = 7.37 (d, 1H), 6.72 (dd, 1H), 6.47-6.26 (m, 3H), 6.23 (d, 1H), 5.31 (d, 1H), 5.13 (d, 1H).

^{13}C NMR ($CDCl_3$ 100 MHz, ppm): δ = 153, 142, 136, 128, 120, 117, 111, 108

Ref: *Org. Biomol. Chem.*, 2010, **8**, 2312-2315; *Chem. Commun.*, 2018, **54**, 10104-10107; *Chem. Eur. J.* 2013, **19**, 3833-3837.