Supporting Information

The interaction between Ru and ZrO_2 delivers a significant impact on the hydroesterification of styrene

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Table S1 Physicochemical properties of ZrO_2 calcined at different temperature

Entry	Supports	S_{BET}[a] ($m^2 \cdot g^{-1}$)	D_p[b] (nm)	V_p[c] ($cm^3 \cdot g^{-1}$)
1	ZrO_2(400)	81	8.5	0.241
2	ZrO_2(500)	60	15.4	0.270
3	ZrO_2(600)	34	15.8	0.215

Notes: [a] specific surface area; [b] pore size; [c] total pore volume.

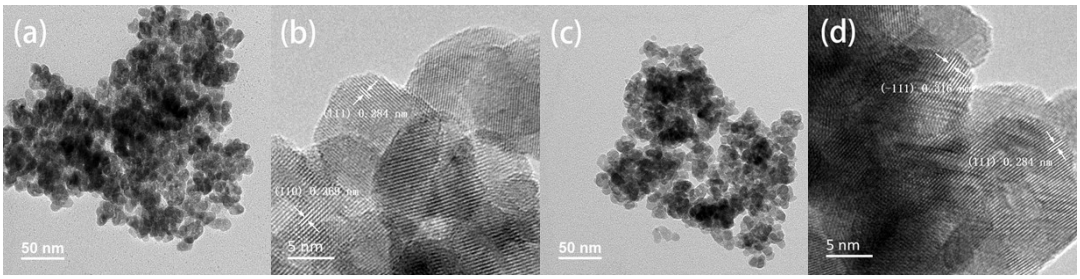

Fig. S1 TEM of reduced catalysts: (a) low- and (b) high-magnification images of 1%Ru(acac)/ZrO_2(400); (c) low- and (d) high-magnification images of 1%Ru(Cl)/ZrO_2(400).

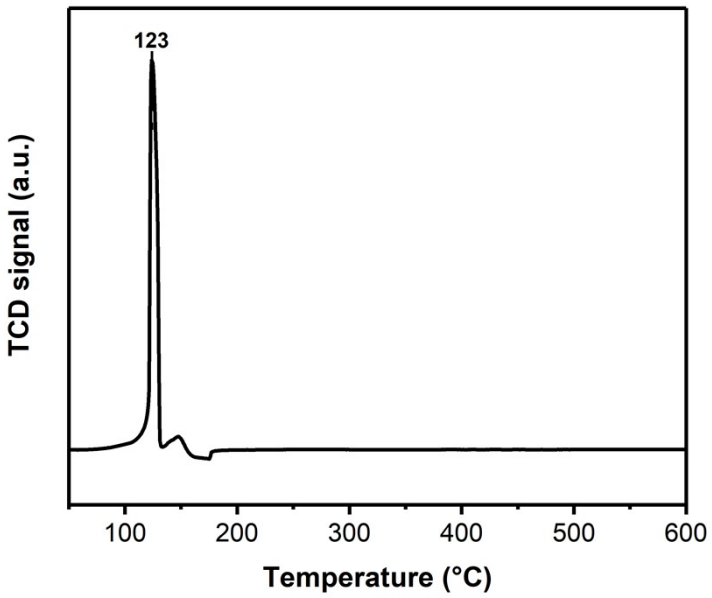

Fig. S2 TPR of ruthenium (III) chloride calcined at 400 ºC

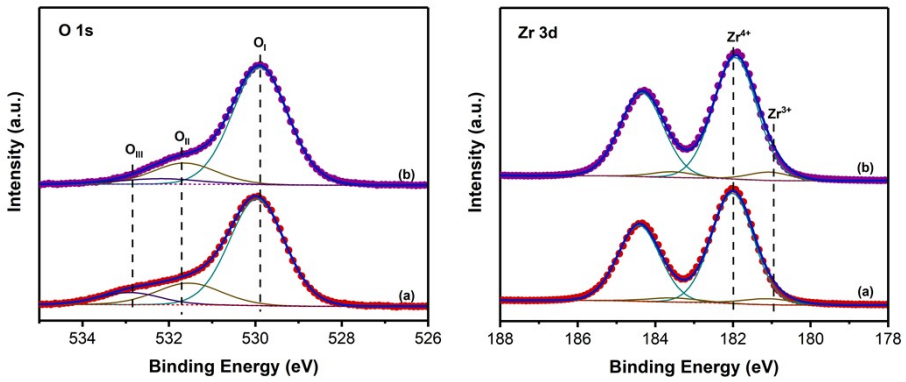

Fig. S3 XPS of O 1s (left) and Zr 3d (right) of the reduced sample: (a) 1%Ru(acac)/ZrO_2(400); (b) 1%Ru(Cl)/ZrO_2(400). O_I, O_{II} and O_{III} are oxygen in the ZrO_2 framework, oxygen vacancies, and adsorbed water, respectively.

Table S2 Chemical compositions of reduced samples[a]

Catalysts	$Ru^{\delta+}/(Ru^0+Ru^{\delta+})$	Zr^{3+}/Zr^{4+}	O_{II}/O_I
1%Ru(acac)/ZrO_2(400)	0.35	0.07	0.23
1%Ru(Cl)/ZrO_2(400)	0.51	0.07	0.22

[a] Calculated from XPS.

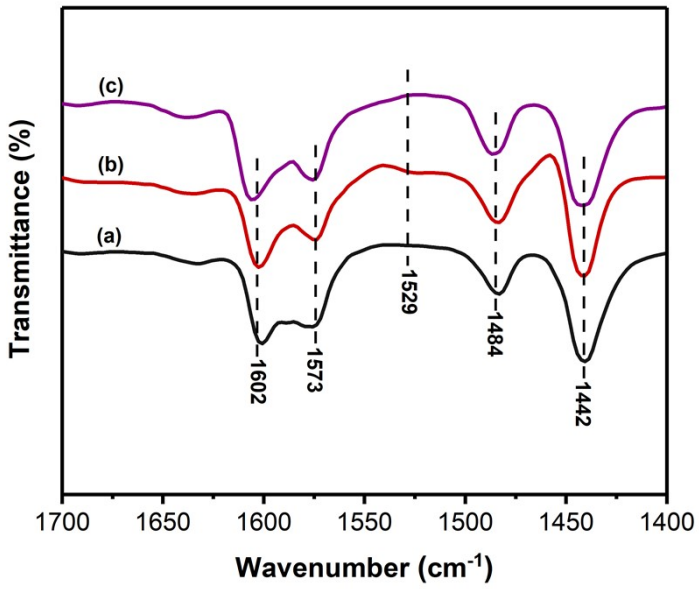

Fig. S4 Pyridine-IR of the sample: (a) ZrO_2(400); (b) 1%Ru(acac)/ZrO_2(400); (c) 1%Ru(Cl)/ZrO_2(400).

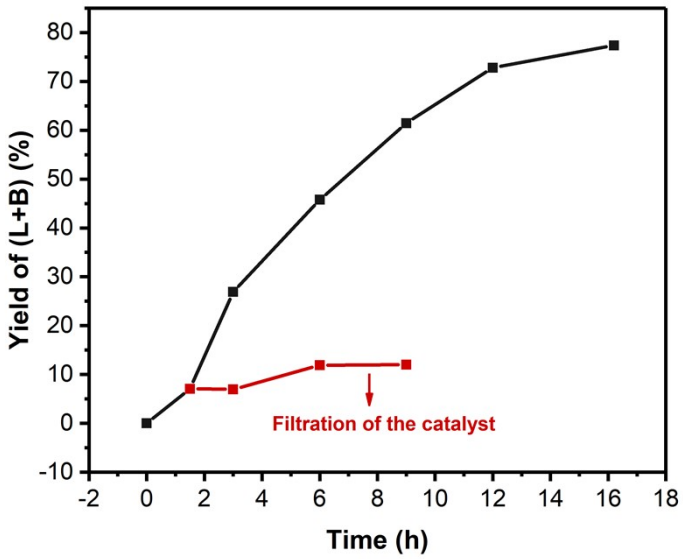

Fig. S5 Filtration reaction. Reaction conditions: 2 mmol styrene, styrene/Ru = 83, 0.1 g n-decane, 5 ml methanol, P = 0.5 MPa, T = 160 ºC.

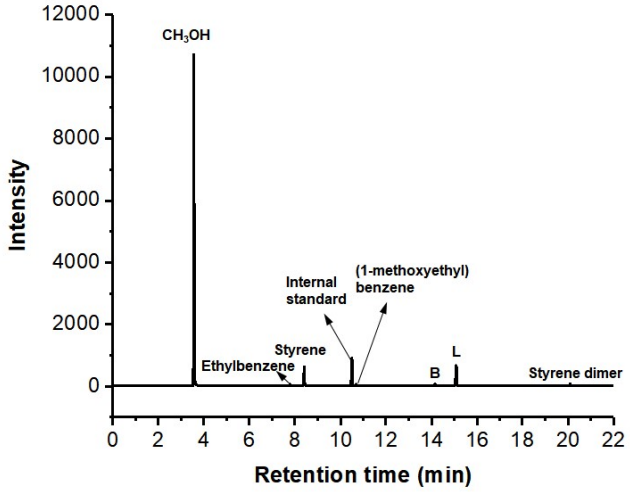

Fig. S6 GC-FID peak analysis of styrene hydroesterification over 1%Ru(Cl)/ZrO_2(400). Reaction conditions: 2 mmol styrene, styrene/Ru = 83, 0.1 g n-decane, 5 mL methanol, P = 0.5 MPa, T = 160 ºC, t = 6 h.

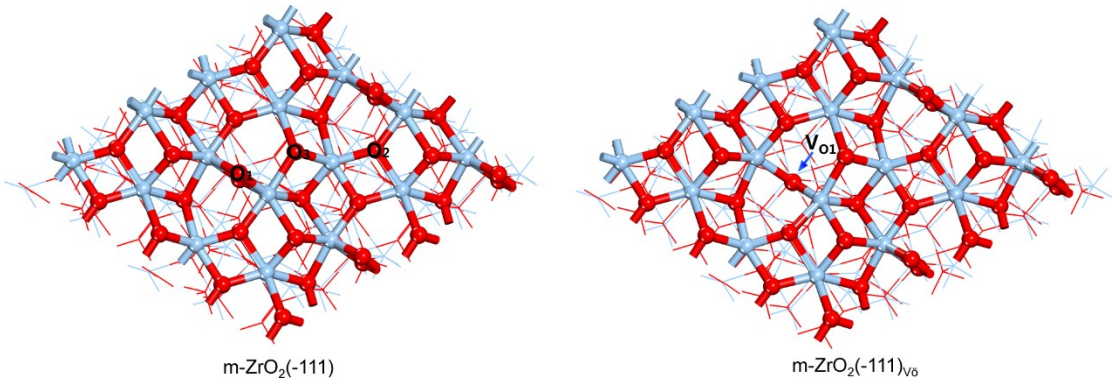

Fig. S7 The optimized geometries of m-ZrO_2(-111) and m-ZrO_2(-111)$_{Vö}$ with the lowest energy.

Table S3 Formation energies $\Delta E_{Vö}$ (in eV) of m-ZrO_2(-111) surface with oxygen vacancies

Entry	Oxygen vacancy	E (eV)	$\Delta E_{Vö}$ (eV)
1	V_{O1}	-132583.5075	5.95
2	V_{O2}	-132583.3829	6.07
3	V_{O3}	-132583.2531	6.20

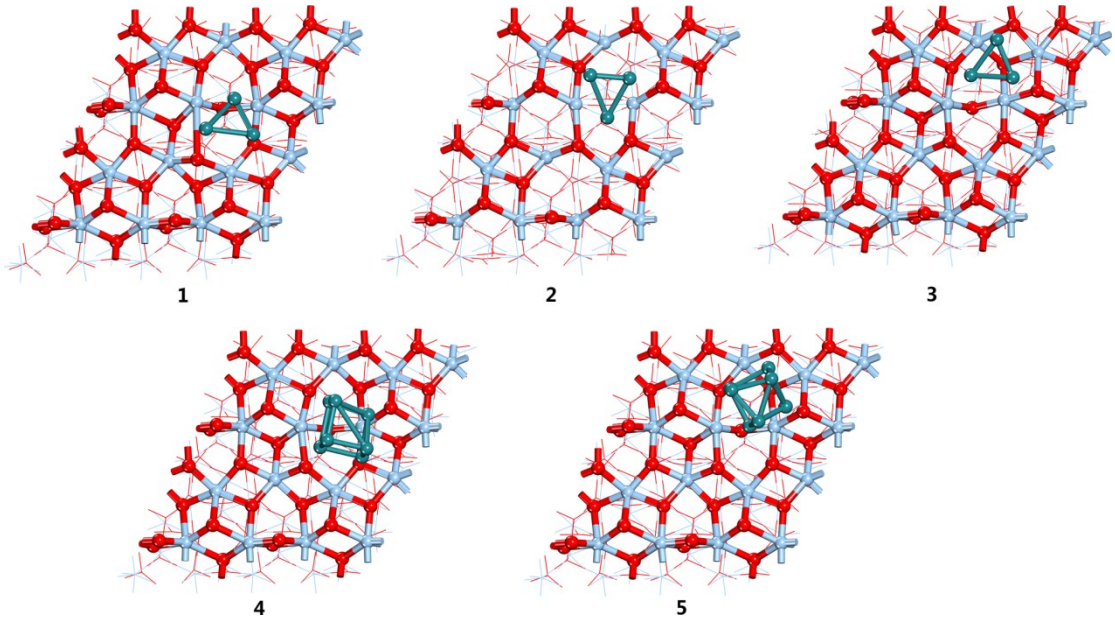

Fig. S8 The optimized geometries of Ru_3 and Ru_7 supported on m-ZrO_2(-111)$_{Vö}$.

Table S4 Adsorption energies of Ru_3 and Ru_7 clusters on m-ZrO_2(-111)$_{Vö}$ surface with oxygen vacancies

Model catalysts	Optimized structures	E (eV)	ΔE (eV)
Ru_3/m-ZrO_2(-111)$_{Vö}$	1	-140385.3396	-7.38
	2	-140384.4597	-6.50
	3	-140384.3323	-6.37
Ru_7/m-ZrO_2(-111)$_{Vö}$	4	-150788.9183	-8.66
	5	-150787.5316	-7.27