Supporting information

Purified CaO supported Pt nanoparticle for the selective hydrogenation of styrene oxide with enhanced selectivity of 1-phenylethanol

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Chemicals

All chemicals used were of analytical grade and not further purified. Calcium fluoride (CaF$_2$), calcium titanate (CaTiO$_3$), magnesium oxide (MgO), strontium oxide (SrO), stannic oxide (SnO$_2$), stannous oxide (SnO), zirconium dioxide (ZrO$_2$), zinc oxide (ZnO), manganese monoxide (MnO) and γ-aluminium oxide (γ-Al$_2$O$_3$) were obtained from Aldrich. Methanol, calcium phosphate (Ca$_3$(PO$_4$)$_2$) and chitosan (CS, deactylation

degree > 90 %) were obtained from Macklin. Palladium chloride ($PdCl_2$) was obtained from Sinopharm Chemical. Titanium dioxide (TiO_2) was obtained from Beijing Entrepreneur Science & Trading Co. Concentrated hydrochloric acid (HCl) was obtained from Xilong Scientific Co.

Catalyst Preparation

Preparation of Pt-based catalysts

CaF_2, SrO, SnO_2 or SnO (5.0 g) was dispersed in 250 mL of acetone, and then prepared Pt colloid (21.2 g) was added dropwise. After stirring for 24 hours, and then the above mixture was centrifuged, which was further washed with acetone for 1 time and was centrifuged. Later, precipitate was dried by vacuum freeze dryer to obtain catalysts with a nominal weight percentage of Pt loading 0.5 %.

$CaTiO_3$, $Ca_3(PO_4)_2$, MgO, TiO_2, ZrO_2, ZnO, MnO or γ-Al_2O_3 (5.0 g) was dispersed in 250 mL of EG, and then prepared Pt colloid (21.2 g) was added dropwise. After stirring for 3 hours, 300 mL of deionized water was poured into above mixture with stirring for 3 hours another. Then, the sample was centrifuged, which was further washed alternately with ethanol absolute and deionized water for 5 times and was centrifuged. Later, precipitate was dried by vacuum freeze dryer to obtain catalysts with a nominal weight percentage of Pt loading 0.5 %.

Preparation of Pd-based catalysts

H$_2$PdCl$_4$ was prepared according to the following procedures. Typically, 1.0 g of PdCl$_2$ was dissolved into 10 mL of HCl. Then 200 mL of deionized water was added, which was further evaporated to last drop of water at 95 °C with repeating this for 3 times. Later, 200 mL of deionized water was added another to obtain H$_2$PdCl$_4$ (0.29 wt%). H$_2$PdCl$_4$ (8.4 g) was placed in a beaker. Then deionized water was injected to tailor the pH value of the system to 4-5 (When MgO was support, pH value was adjusted to 6), following which 5.0 g of MgO, ZnO, TiO$_2$ or γ-Al$_2$O$_3$ support was added. Thereafter, the liquid was dried by evaporating with stirring at 95 °C. Next, the dried solid was reduced by flowing H$_2$ for 1 hour, which was further washed with deionized water for 3 times and was centrifuged. Later, the sample was dried by vacuum freeze dryer to obtain catalysts 0.5Pd/MgO, 0.5Pd/ZnO, 0.5Pd/TiO$_2$ or 0.5Pd/γ-Al$_2$O$_3$.

Preparation of Pd/Chitosan (Pd/CS) catalysts

The Pd/CS catalysts were prepared according to the method in literature but with some minor modifications. [S1] PdCl$_2$ (0.0729 g) was dissolved in ethanol (46 mL) and a drop of HCl. Then Chitosan (CS, 4.30 g) was added into the above mixture and stirred continuously for 72 h at room temperature. The mixture was centrifuged and washed with ethanol and then suspended in ethanol for 5 h reflux in flowing N$_2$, after which the mixture was centrifuged and dried with vacuum freeze dryer. Next, the above sample was reduced with NaBH$_4$ (0.55 g, more than 35 times the molar amount of Pd) at room temperature for 4 h under nitrogen atmosphere. Finally, the sample was centrifuged and washed with deionized water for 4 times, which was further dried with vacuum freeze dryer to obtain dark gray catalysts 1Pd/CS.

The ex-situ FT-IR spectra of SO over the catalysts

The *ex-situ* FT-IR spectra of SO adsorbed on the catalysts was carried out over Perkin Elmer Spotlight i200. The catalysts, including Pt/CaO-P, Pt/CaCO$_3$ and Pt/TiO$_2$, were immersed in pure SO for a duration of three hours to achieve saturation adsorption. Subsequently, the catalysts were centrifuged and treated with flowing Ar gas for twelve hours at a temperature of 60°C to eliminate the physically adsorbed SO. The resultant sample was mixed with KBr powder, thoroughly ground, and pressed into a wafer. The sample was then measured in the range of 4000 cm^{-1} to 450 cm^{-1} with a reference wafer containing the same catalyst and KBr to collect the background IR spectrum.
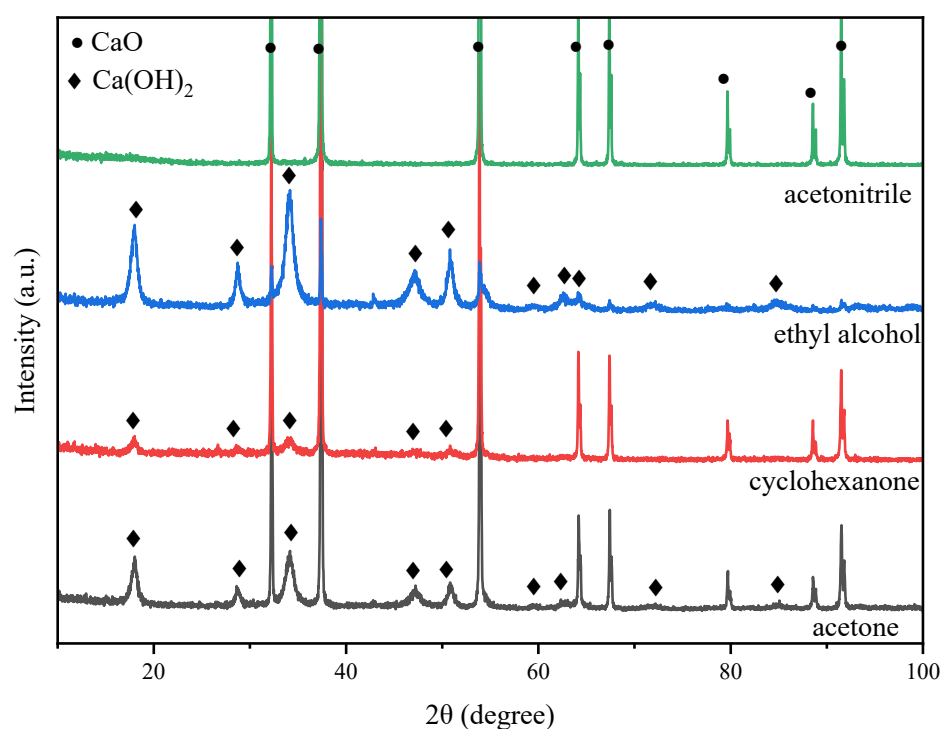
Fig. S1. The XRD patterns of preparing 0.5Pt/CaO catalysts with different solvent.
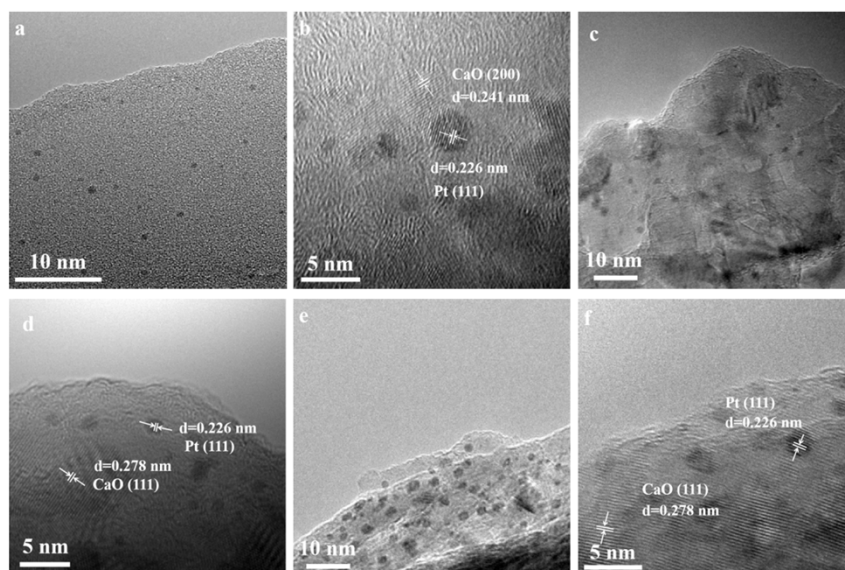
Fig. S2. The HRTEM images of (a, b) 0.1Pt/CaO-P, (c, d) 0.3Pt/CaO-P and (e, f) 0.7Pt/CaO-P. The HRTEM images of Pt nanoparticles in the corresponding supports.

As shown in Table R1, for the 2Pt/CaCO$_3$ catalyst, the XPS results showed that atomic percentage of Pt (6.06 at%) is higher than the theoretical value (0.21 at%), and a similar situation was found on the 2Pt/CaO-P catalyst, indicating that most of Pt nanoparticles located on the outer surface of the supports of CaO-P and CaCO$_3$. However, for the 2Pt/Ca(OH)$_2$ catalyst, the surface concentration of Pt (0.13 at%) was lower than its theoretical value (0.32 at%), which suggested that part of the Pt might be loaded in the pores of Ca(OH)$_2$.

Table S1 The loading percentages of Pt in the catalysts measured with ICP-OES.

Catalyst	Pt with ICP-OES (wt%)
0.5Pt/CaO-P	0.29
0.5Pt/CaO	0.36
0.5Pt/Ca(OH)$_2$	0.38
0.5Pt/CaCO$_3$	0.35
0.1Pt/CaO-P	0.065
0.3Pt/CaO-P	0.18
0.7Pt/CaO-P	0.43

Table S2 The surface concentration, binding energy and portion of different states of Pt in the catalysts measured with XPS.

Catalyst	Pt surface concentration with XPS (At%)	Theoretical Pt (At%)	Pt^0 (eV)	PtO (eV)	portion of PtO in total surface Pt content (%)
2Pt/CaO-P	0.50	0.29	70.8	72.2	31.4%
2Pt/Ca(OH)$_2$	0.13	0.32	70.9	72.0	21.2%
2Pt/CaCO$_3$	6.06	0.21	71.3	-	-

The loading percentage of Pt in Pt/CaO-P was optimized as Table S3 shown. Under the same reaction condition, the conversion of SO over 0.1Pt/CaO-P was lowest, and the conversions of SO over 0.3Pt/CaO-P and 0.7Pt/CaO-P can reach 92.7% and 97.6%, respectively. Though the conversion of SO over 0.5Pt/CaO-P (87.3%) was lower than that over 0.3Pt/CaO-P and 0.7Pt/CaO-P, the selectivity of 1-PEA was higher than that over other three catalysts. Therefore, the optimized loading percentage of Pt is 0.5 wt%.

Table S3 The influence of Pt loading percentages on the catalytic performance of the catalysts.

Catalyst	Conversion (%)	Selectivity (%)			
		2-PEA	1-PEA	EB	2-CYHE
0.1Pt/CaO-P	59.2	45.0	36.0	14.7	0
0.3Pt/CaO-P	92.7	48.0	34.4	12.2	0.5
0.5Pt/CaO-P	87.3	48.9	39.1	10.8	0.6
0.7Pt/CaO-P	97.6	47.5	34.3	14.5	0.7

Reaction conditions: The mass of the catalyst, 0.65 g; S/C, 50:1; stirring rate, 500 rpm; temperature, 90 °C; the pressure of hydrogen, 2 MPa; reaction time, 8 h. EB, ethylbenzene; 2-CYHE.

The dependence of the catalytic performance on the concentration of SO was investigated to explore the influence of the number of the surrounding SO per unit catalyst on the selectivity. As the concentration of SO increased from 0.3 mg ml^{-1} to 3.3 mg ml^{-1}, the b:l value (branched product: linear product) increased from 0.52 to 0.80, and the further increased concentration can lead to the decrease of b:l value (Table S4). The results reveal that the compatibility between the concentration of SO and the catalyst is very important for the production of 1-PEA.

Table S4 The dependence of the catalytic performance on the concentration of SO.

Concentration (mg/ml)	b:l (1-PEA:2-PEA)	Selectivity (%)		
		2-PEA	1-PEA	EB
0.3	0.52	57.1	30.0	15.8
1.1	0.60	50.9	30.7	15.9
3.3	0.80	48.9	39.1	10.8
10	0.63	58.7	36.8	9.1
33	0.51	62.5	32.1	8.4

Reaction conditions: catalyst, 0.5Pt/CaO-P; the mass of the catalyst, 0.65 g; temperature, 90 °C; stirring rate, 500 rpm; the pressure of hydrogen, 2 MPa.

Table S5 The catalytic performance of the metal oxides support Pt or Pd in the selective hydrogenation of SO.

Catalyst	Temperature (°C)	Time (h)	Conversion (%)	Selectivity (%)				
				2-PEA	1-PEA	EB	SM	2-CYHE
0.5Pt/MgO	60	2	85.9	77.8	6.6	5.2	0	7.3
0.5Pt/CaO	90	8	99.1	71.2	17.2	6.1	0	2.6
0.5Pt/SrO	90	8	5.2	50.2	22.4	8.7	18.2	0
0.5Pt/SnO$_2$	60	2	65.1	86.2	1.1	4.7	0	4.3
0.5Pt/SnO	60	2	11.9	85.0	2.6	9.8	0	0
0.5Pt/TiO$_2$	60	2	99.6	29.0	0.3	20.4	0	28.0
0.5Pt/ZrO$_2$	60	2	99.9	22.7	0	13.0	0	55.2
0.5Pt/ZnO	60	2	68.7	83.3	0.4	2.8	7.8	0
0.5Pt/MnO	60	2	38.5	68.9	1.8	3.7	21.3	0
0.5Pt/Al$_2$O$_3$	60	2	99.5	33.6	0.4	8.4	0	34.1
0.5Pd/MgO	60	2	98.9	73.0	0.8	0.5	0	0
0.5Pd/TiO$_2$	60	2	99.8	93.0	1.0	0.8	0	0
0.5Pd/ZnO	60	2	99.5	95.7	1.1	0.6	0	0
0.5Pd/Al$_2$O$_3$	60	2	99.9	88.2	1.0	0.6	0	0.03
0.5Pt/CaF$_2$	90	8	15.9	79.9	4.4	11.3	0	0
0.5Pt/Ca$_3$(PO$_4$)$_2$	90	8	68.5	81.0	4.7	5.8	0	0.7
0.5Pt/CaTiO$_3$	60	2	99.6	71.0	1.2	2.7	0	21.1
1Pd/CS	70	2	100	94.0	0.8	0.9	0	0

Reaction conditions: The mass of SO, 0.1g; solvent, cyclohexane; stirring rate, 500 rpm; the pressure of hydrogen, 2 MPa; the molar ratio of substrate to catalyst (S/C), 100:1.
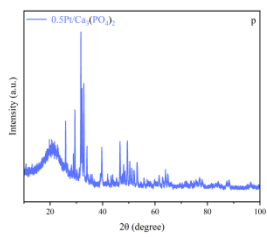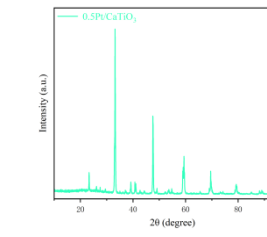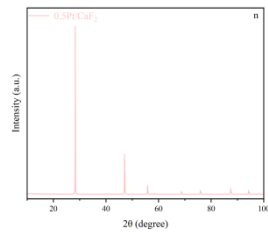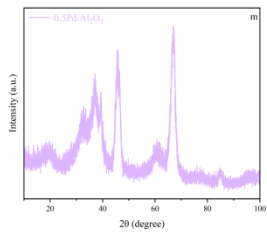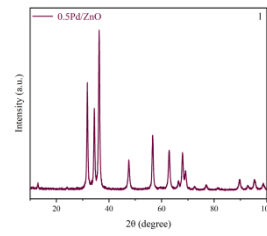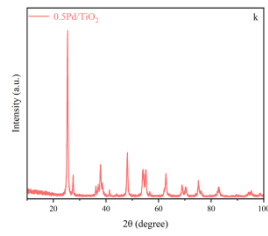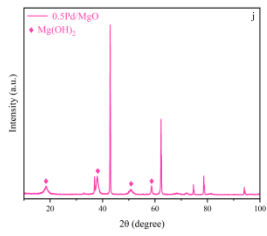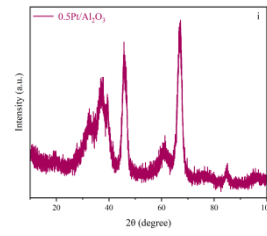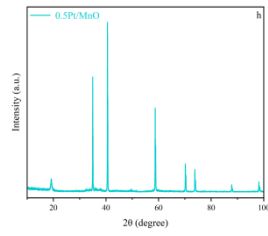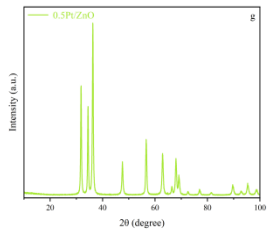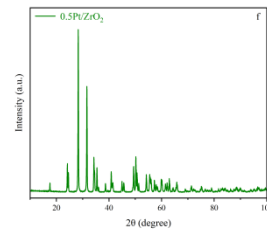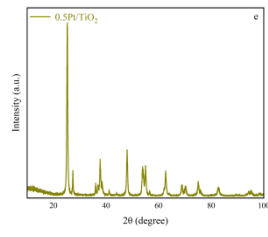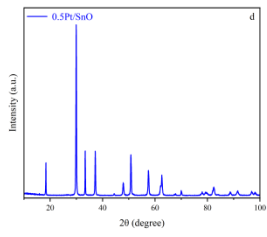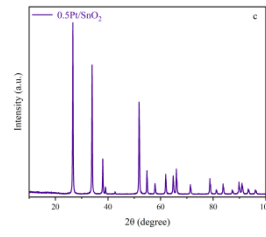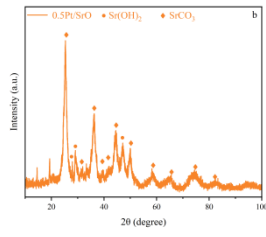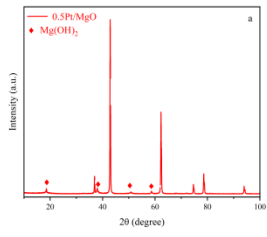
Fig. S3. The XRD patterns of (a) 0.5Pt/MgO, (b) 0.5Pt/SrO*, (c) 0.5Pt/SnO$_2$, (d) 0.5Pt/SnO, (e) 0.5Pt/TiO$_2$, (f) 0.5Pt/ZrO$_2$, (g) 0.5Pt/ZnO, (h) 0.5Pt/MnO, (i) 0.5Pt/Al$_2$O$_3$, (j) 0.5Pd/MgO, (k) 0.5Pd/TiO$_2$, (l) 0.5Pd/ZnO, (m) 0.5Pd/Al$_2$O$_3$, (n) 0.5Pt/CaF$_2$, (o) 0.5Pt/CaTiO$_3$ and (p) 0.5Pt/Ca$_3$(PO$_4$)$_2$.
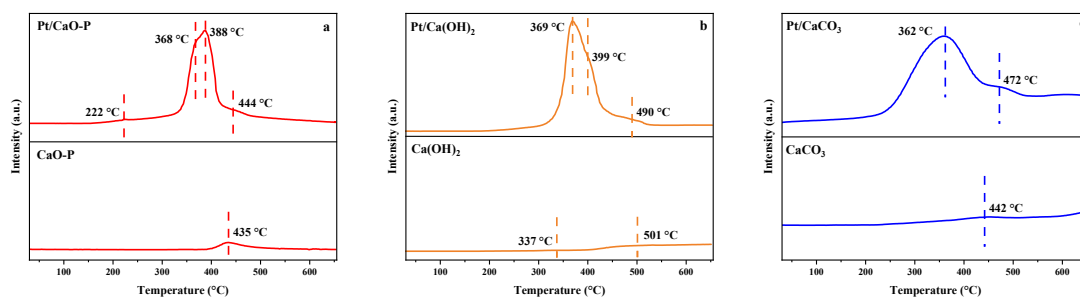

Fig. S4. The H$_2$-TPD curves over (a) CaO-P and Pt/CaO-P, (b) Ca(OH)$_2$ and Pt/Ca(OH)$_2$, (c) CaCO$_3$ and Pt/CaCO$_3$.
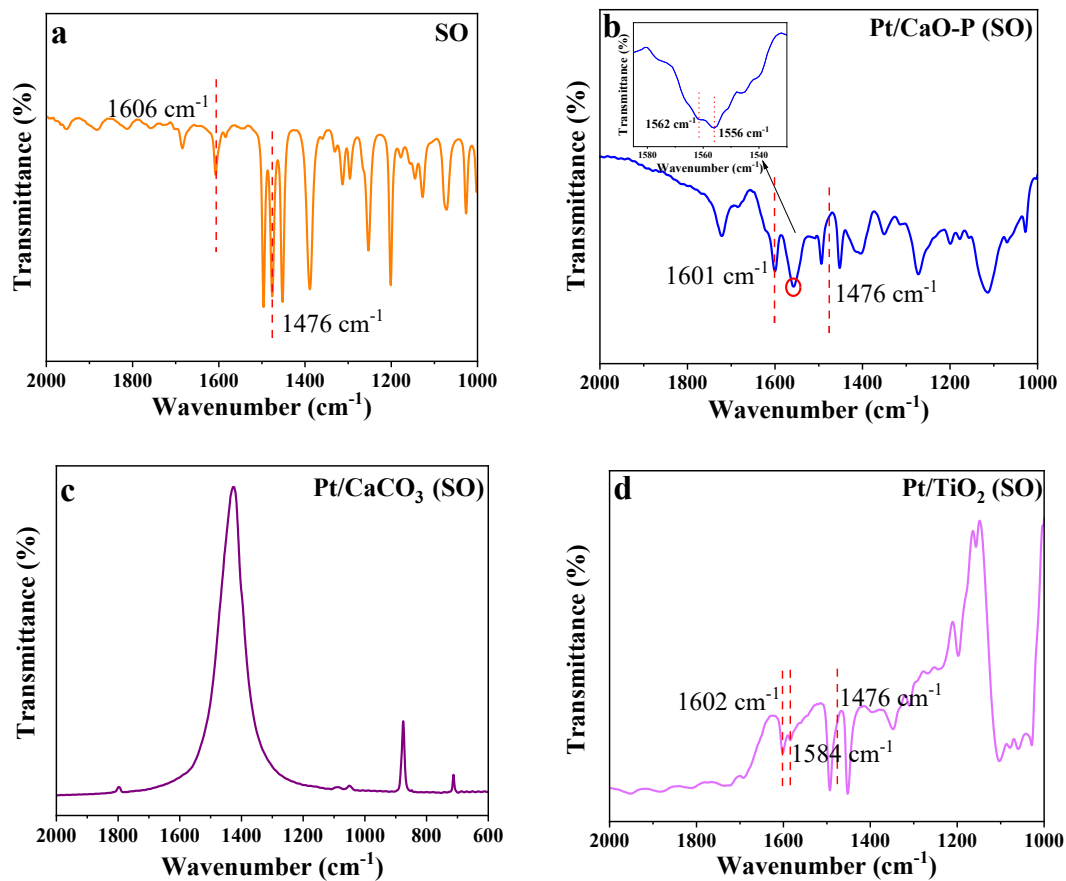
Fig. S5. The FTIR spectra of (a) SO molecule, SO adsorbed on (b) Pt/CaO-P, SO adsorbed on (c) Pt/CaCO$_3$ and (d) Pt/TiO$_2$. The insert in (b) is the fine curve of SO adsorbed on Pt/CaO-P.

Reference

[S1] M. Viswanadhan, A. Potdar, A. Divakaran, M. Badiger and C. Rode, Res. Chem. Intermediat., 2016, **42**, 7581-7595.