

Supplementary Information

Pt-FeO_x/SiO₂ catalysts prepared by galvanic displacement show high selectivity for cinnamyl alcohol production in the chemoselective hydrogenation of cinnamaldehyde

Yu-Sheng Shi, Zi-Fei Yuan, Qian Wei, Ke-Qiang Sun* and Bo-Qing Xu*

Innovative Catalysis Program, Key Lab of Organic Optoelectronics & Molecular Engineering,
Department of Chemistry, Tsinghua University, Beijing, 100084, China.

1 Experimental

1.1 Catalyst preparation

Fe/SiO₂ samples with three different Fe loadings (3.7%, 5.3%, 11.6%) were prepared by a deposition-precipitation method. Different loadings of Pt was added to the above Fe/SiO₂ by a galvanic replacement method.

A typical procedure of preparing the Fe/SiO₂ is as follows. A defined amount of Fe(NO₃)₃ • 9H₂O (99.5%, Acros) was dissolved in 300 mL deionized water, adjusted to yield 3.7, 5.3, 11.6 wt.% of Fe in the final Fe/SiO₂ samples and 3g of SiO₂ (200 m²/g, Degussa) was suspended in the Fe(NO₃)₃ solution. After that, urea was added to make its concentration ten times higher than Fe(NO₃)₃. The suspension was heated to 80 °C and kept vigorous stirring for 2h, followed by 5h aging at room temperature under stirring. The solid was centrifuged and washed with 200 mL deionized water for 3 times. Then, it was dried in a vacuum oven at 70 °C overnight and calcinated at 500 °C for 2h in order to make all the nitrates decompensate. The obtained samples are denoted as “mFe/SiO₂” in which “m” refers to Fe loading (wt%) according to XRF measurement.

The obtained Fe/SiO₂ was reduced to form supported Fe nanoparticles at 700 °C according to H₂-TPR results. A deaerated aqueous solution of Pt(NH₃)₄(NO₃)₂ (99.5%, Alfa) was then added into the freshly reduced Fe/SiO₂ under Ar bubbling to protect the sample from exposing to air. The higher standard reduction potential of Pt²⁺/Pt pair than that of Fe²⁺/Fe (0.12V vs. -0.441V) enables the occurring of galvanic replacement reaction, leading to the preferential deposition of Pt on Fe particles via partial replacement of the surface Fe atoms. The solid was separated by filtration, washed and then dried at 110 °C. The obtained samples were denoted as xPt-yFeO_x/SiO₂, where “x” and “y” represents the loading (wt%) of Pt and Fe, respectively, according to XRF measurement.

1.2 Characterization

X-ray photoelectron spectroscopy (XPS) has been used to determine the surface content of elements and was carried out on a SKL-12 instrument using Mg K α radiation (1253.6 eV). The bindingenergies (BE) were calibrated using the adventitious C 1s line at 284.8 eV. The Ar ion bombardment of the samples was performed in the XPS spectrometer. Acceleration voltages were 10kV and bombarded about 1nm each time. XPS study was carried before and after every time of bombardment.

X-ray diffraction (XRD) patterns were collected on a Bruker D8 Advance X-ray diffractometer using Cu K α ($\lambda = 0.15406$ nm) radiation source at 40 kV and 40 mA. All the spectra were recorded at 20° ~ 90° with a scan rate of 6° • min⁻¹. The average crystallite sizes were calculated according to Scherrer equation, $D = 0.90\lambda/\beta\cos\theta$, where θ is the diffraction angle and β is the full width at the half-maximum (FWHM).

Quantitative temperature-programmed reduction (TPR) of the samples were conducted up to 800 °C and held at this temperature for 30 min with 5% H₂/Ar as the reductant. The temperature ramp was 10 °C/min. Water was removed from the exit gas with a cold trap at -85°C to avoid its interference into the TCD detector. Before the

reduction, samples were pretreated at 110 °C with Ar flow of 40 mL/min for 30min.

CO pulse chemisorption test was conducted in a ASAP 2010 Micromeritics at 50 °C by a pulse injection method. In principle, samples were first pretreated with the same method before catalytic reactions, then purged with Ar for 30 min. CO (0.48 cm³) were injected into the tube pulse by pulse after the sample was cooled to 50 °C till the signal of CO didn't have significant change (deviation of the signal was less than 5%) for continuous 5 pulses. The whole process was detected by a MS. In calculating Pt dispersion from CO chemisorption data, it was assumed that CO was chemisorbed in a line form over Pt atoms.

1.3 Hydrogenation reaction of CAL

Hydrogenation of cinnamaldehyde (CAL) was chosen as probe reaction to investigate catalytic properties of the prepared catalysts. It was performed in a high-pressure batch reactor with 50 mL autoclave made by stainless steel. Unless specified, the reaction was performed under the following conditions: 0.5 mL CAL(AR, Sigma-Aldrich) was dissolved in 5mL of toluene (HPLCR, Beijing Chemical Reagent Company) and 50 mg of catalyst was added, after purging with H₂(~0.8MPa) six times, the autoclave was pressurized to a desired pressure (e.g., 1.0MPa) at room temperature. The magnetic stirring was begun(900rpm) by the time when the autoclave was heated to a certain temperature (e.g., 150 °C) and then started timing. The autoclave was cooled in an ice-water bath at the end of reactions. After that, the reacted liquid was separated from catalyst powder by filtration and analyzed by a HP-7890A gas chromatograph (GC) equipped with a Shimadzu HiCap CBP20 capillary column and a flame ionization detector.

2 Results

The absence of diffusion limitation and mass transfer effect under the reaction conditions was checked using the method below.

Table SI1 Effect of Stirring Speed on the Hydrogenation of Cinnamaldehyde over 1.0Pt-5.3FeO_x/SiO₂-GD^a

Stirring speed (rpm)	CAL hydrogenation reaction			
	Conv. (%)	Sel. (%)		
		H _{CAL}	H _{COL}	COL
300	30	3	5	92
500	36	3	3	94
900	36	6	4	90
1200	35	5	3	92

^a P_{H₂} = 1.0 MPa; CAL = 4 mmol; catalyst amount 50.0 mg, 5 mL toluene as solvent, reaction temperature=150 °C

The conversion didn't change significantly after the stirring speed was increased to above 500 rpm. We chose 900rpm as the default speed in order to avoid the diffusion limitation.

Table SI2 Effect of solvent proton activity during galvanic displacement reaction on the performance of final catalysts for cinnamaldehyde hydrogenation.^a

Catalysts	Solvent	CAL hydrogenation reaction			
		Conv. (%)	Sel. (%)		
			H _{CAL}	H _{COL}	COL
0.4Pt-2.7FeO _x /SiO ₂ -GD	ethanol	21	9	3	88
0.7Pt-4.7FeO _x /SiO ₂ -GD	ethanol	44	6	3	91
0.5Pt-4.8FeO _x /SiO ₂ -GD	IPA	22	7	6	87

^a P_{H₂} = 1.0 MPa; CAL = 4 mmol; catalyst amount 50.0 mg, 5 mL toluene as solvent, reaction temperature=150 °C

Table SI3 quantified XPS results.

Sample name	Pt			Pt/Fe _(XPS)	Pt/Fe _(XRF)
	Pt4f _{7/2} [δ+] (ev)	Pt4f _{7/2} [II] (ev)	Pt[δ+]:Pt[II] (at. %)		
0.4Pt-11.3FeOx/SiO ₂ -GD	72.44	74.74	57: 43	0.109	0.010
0.4Pt-5.0FeOx/SiO ₂ -GD	72.32	73.94	64: 36	0.235	0.023
1.0Pt-5.3FeOx/SiO ₂ -GD	72.40	74.00	67: 32	0.271	0.055
1.1Pt-11.0FeOx/SiO ₂ -GD	72.50	74.80	57: 43	0.137	0.028
1.0Pt-5.3FeOx/SiO ₂ -IMP	71.47	73.45	58: 42	0.175	0.060

Table SI4 Quantified XPS results after two successive ten-second Ar⁺ sputterings of 1.0Pt-5.3FeO_x/SiO₂-GD.

Sputtering	Pt			Pt/Fe _(XPS)	Pt/Fe _(XRF)
	Pt4f _{7/2} [δ+] (ev)	Pt4f _{7/2} [II] (ev)	Pt[δ+]:Pt[II] (at. %)		
0	72.18	73.53	41: 59	0.27	0.055
1	72.31	73.82	55 : 45	0.21	0.055
2	71.90	73.25	40: 60	0.19	0.055

Table SI5 Optimization of the catalytic performance of 1.0Pt-5.3FeO_x/SiO₂-GD for cinnamaldehyde hydrogenation. ^a

CALCont. (mL)	H ₂ (MPa)	Rxn Time (h)	CAL hydrogenation				
			Conv. (%)	Sel. (%)			
				HCAL	HCOL	COL	OTHER
0.5	1	2	41	7	1	92	0
1.5	1	40	85	1	2	95	2
1.5	1	48	99	1	2	95	2
1.5	2	16	81	2	2	94	2
1.5	2	20	99	1	2	95	2

^a catalyst amount 50.0 mg, 5 mL toluene as solvent, reaction temperature=150 °C

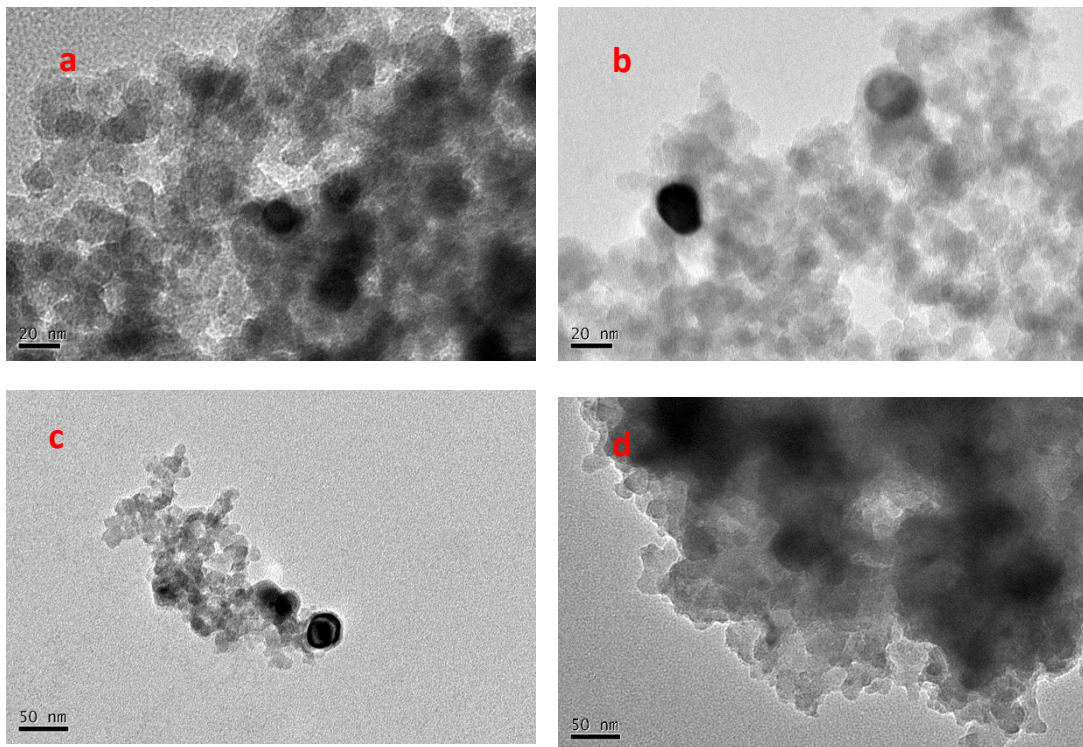


Fig S11 TEM images of (a) 3.7Fe/SiO₂, (b) 5.3Fe/SiO₂, (c) 11.5Fe/SiO₂ and (d) 1.0Pt-5.3FeO_x/SiO₂

The average size of Fe particle on 3.7Fe/SiO₂, 5.3Fe/SiO₂ and 11.5Fe/SiO₂ are 19.6±2.8 nm, 22.9±2.8 nm and 28.9±3.8 nm, respectively. These values are in line with the size determined from XRD diffraction of Fe(110) planes.

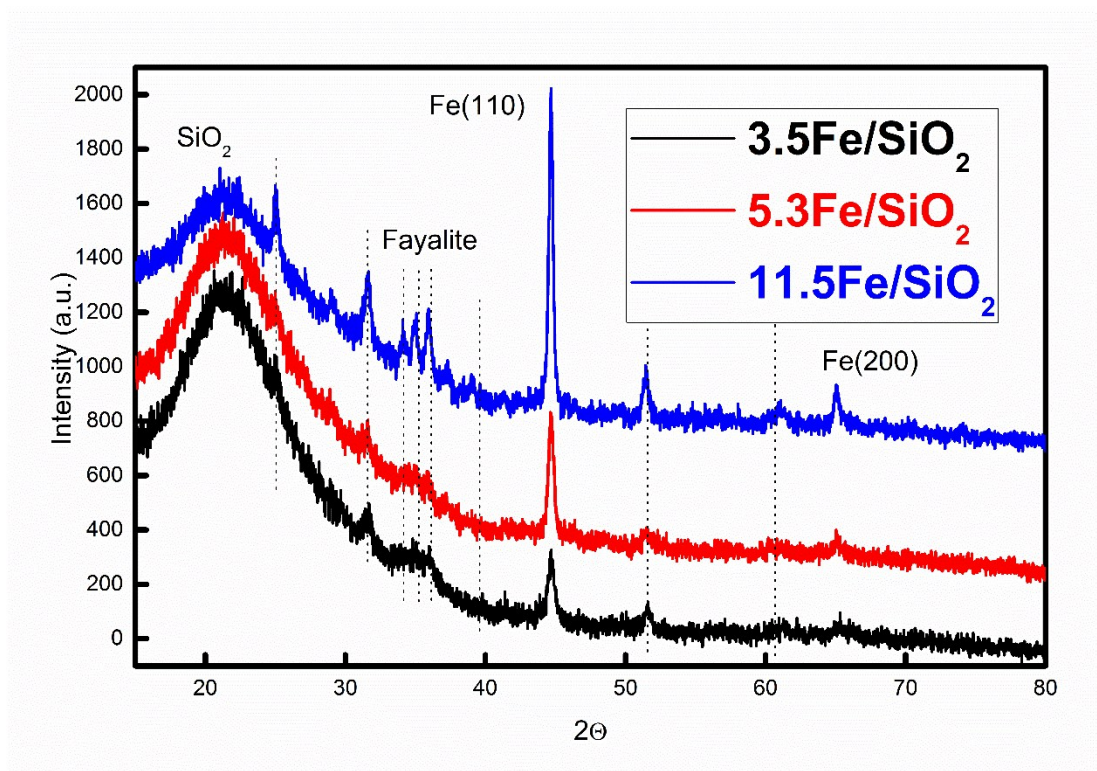


Fig S12 XRD patterns of (a) 3.7Fe/SiO₂, (b) 5.3Fe/SiO₂, (c) 11.5Fe/SiO₂.

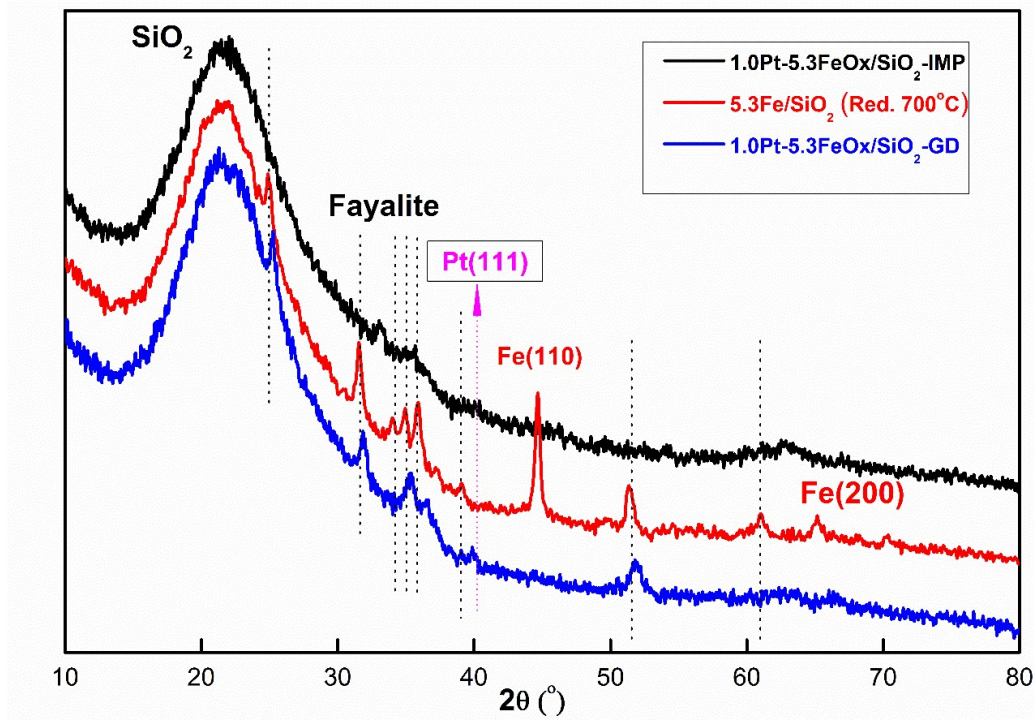


Fig. S13 XRD patterns of (a)1.0Pt-5.3FeO_x/SiO₂-IMP; (b)5.3Fe/SiO₂; (c)1.0Pt-5.3FeO_x/SiO₂-GD

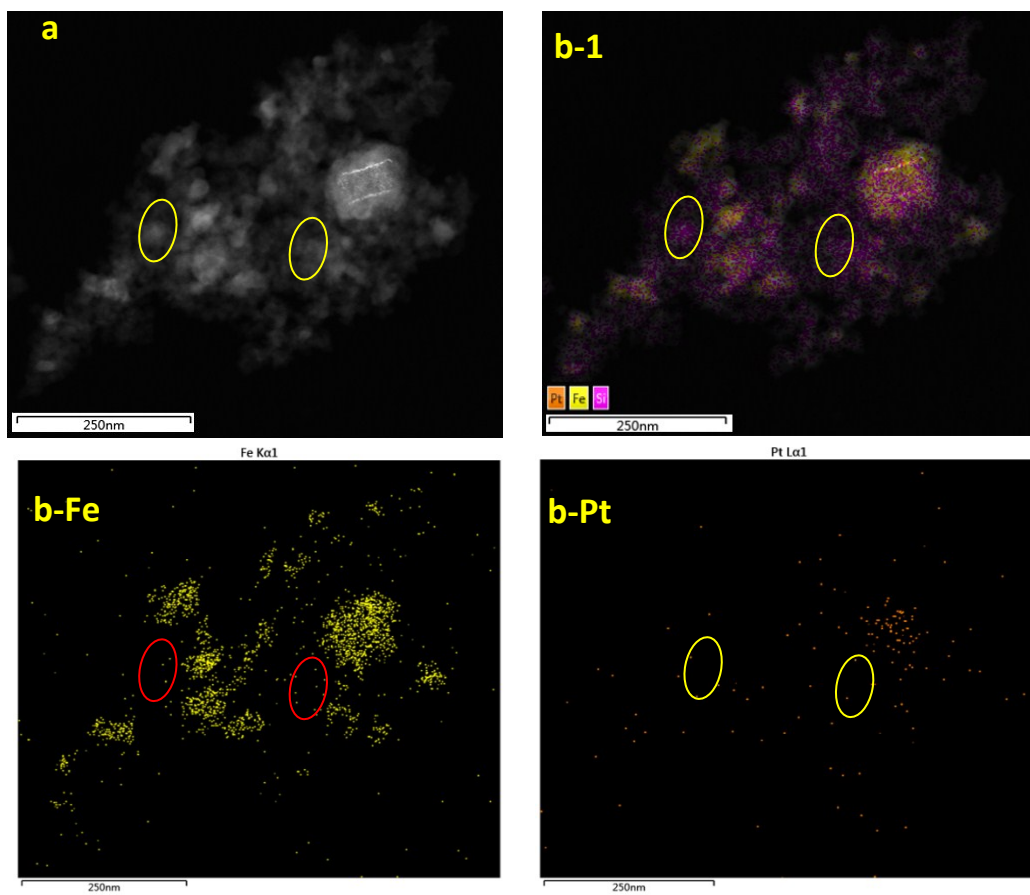


Fig. SI4 (a)HAADF-STEM image of 1.1Pt-11.3FeO_x/SiO₂-GD sample. (b)STEM-EDS elemental mapping images for (a). The circled area indicates the locations free of Fe and Pt.

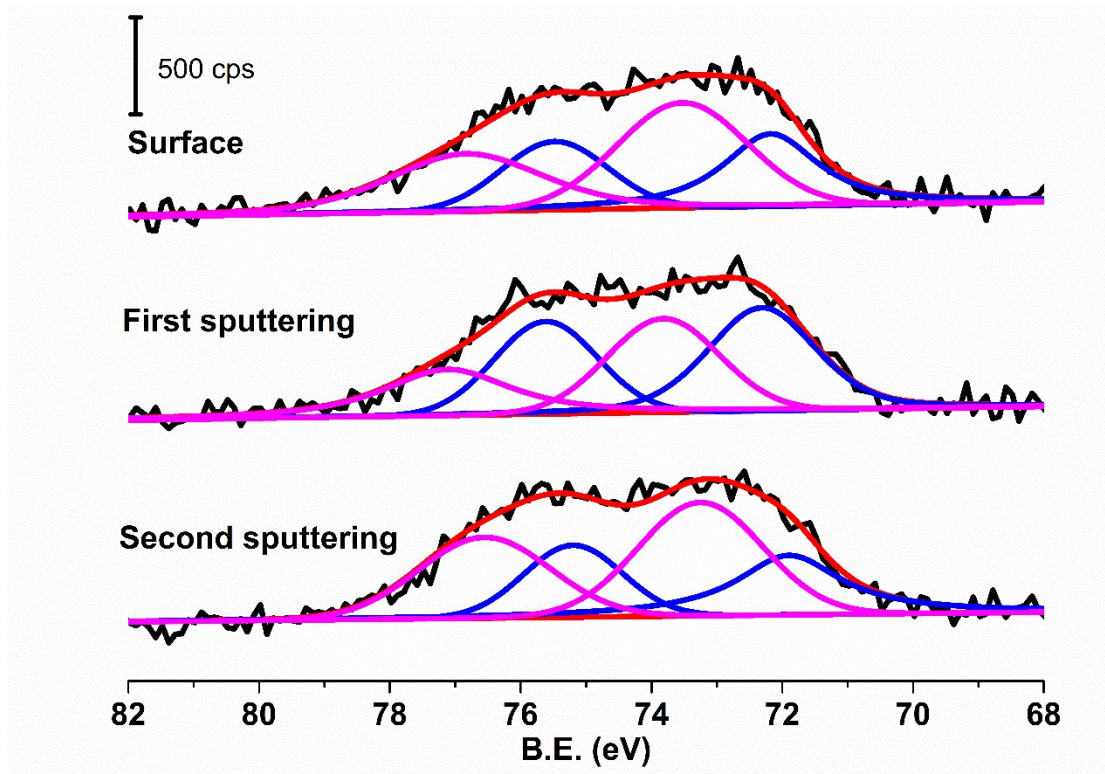


Fig. SI5 Ar^+ sputtering XPS patterns of $1.0Pt-5.3FeO_x/SiO_2-GD$

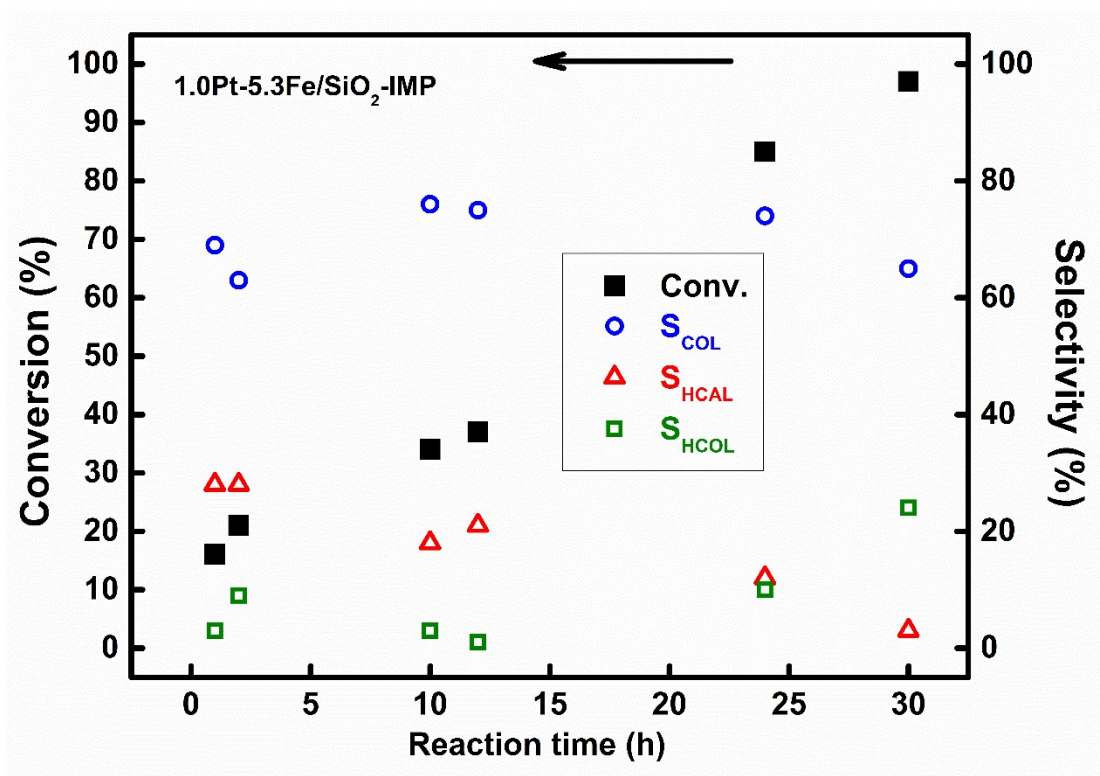


Fig. SI6 The time-course of CAL hydrogenation over 1.0Pt-5.3FeO_x/SiO₂-IMP catalyst.

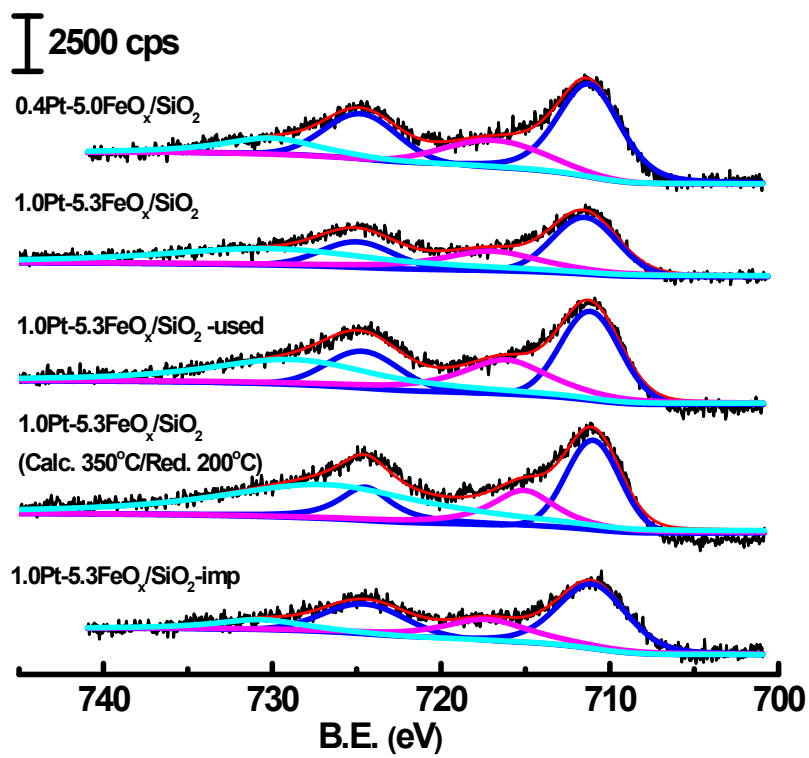


Figure S17. Fe XPS spectra of Pt-FeO_x/SiO₂ samples.