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Supporting Information

Designed Precursor for the Controlled Synthesis of Highly Active Atomic and Sub-nanometric Platinum Catalysts on Mesoporous Silica

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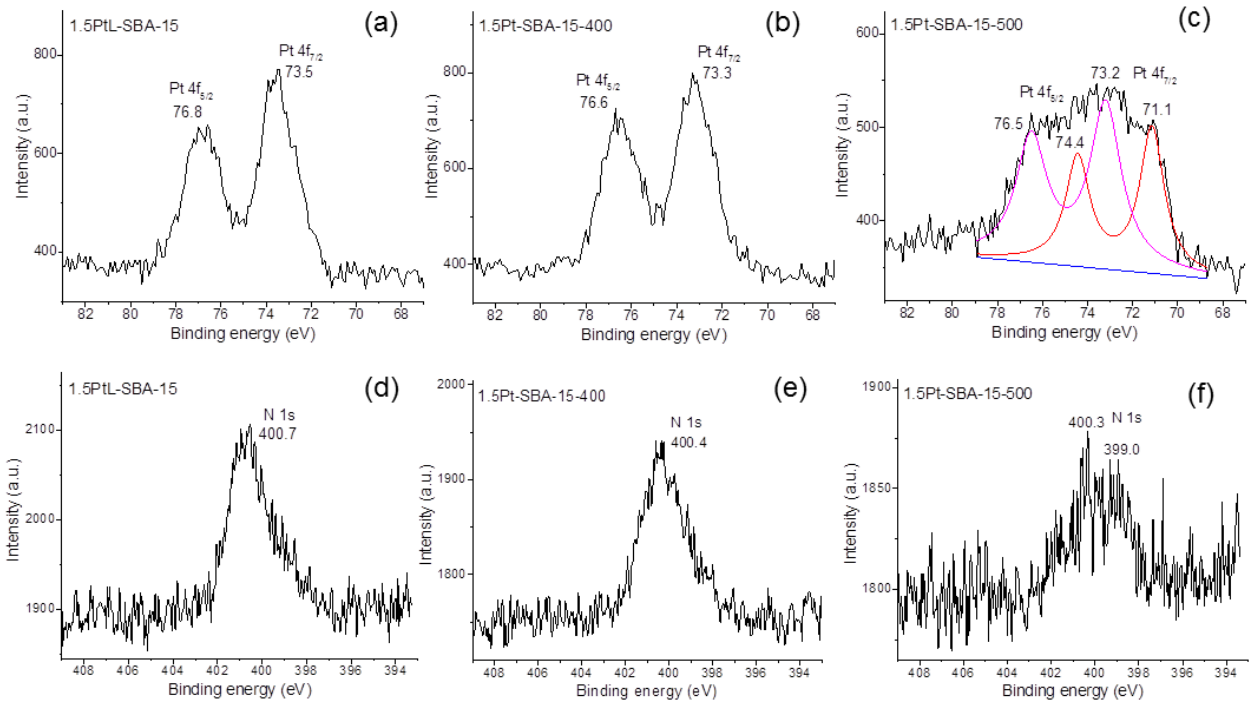


Fig. S1 XPS spectra of SBA-15 supported Pt-complex (1.5 wt% Pt loading) at different temperature: (a, d) before the heat treatment, (b, e) 400 °C, (c, f) 500 °C.

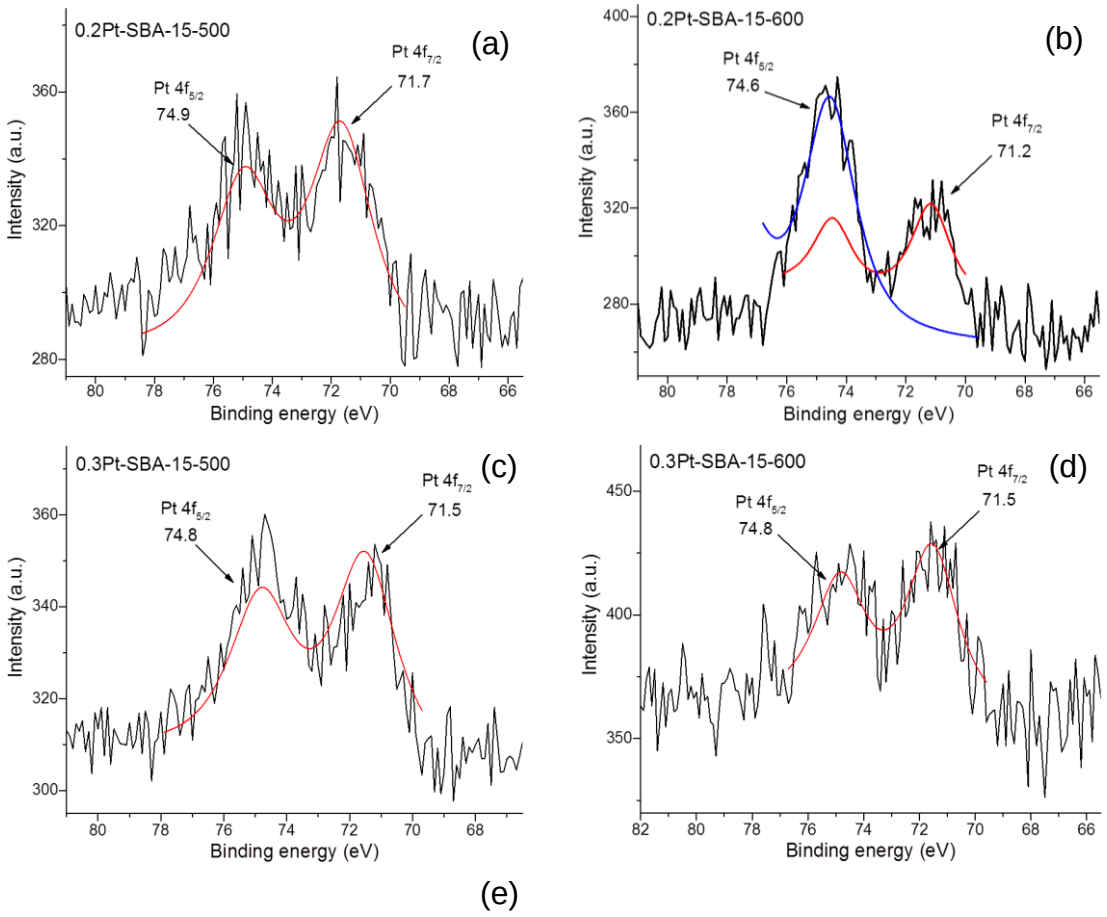
Table S1 Elemental analysis results of samples treated at different temperature.

Sample	**C (%)**	**H (%)**	**N (%)**
SBA-15	ND	1.3	-
1.5PtL-SBA-15	2.49	1.74	0.65
1.5Pt-SBA-15-400	1.67	1.43	0.71
1.5Pt-SBA-15-500	<0.50	1.25	0.52
ND: not detected due to very low carbon content.			

Table S2 Nitrogen content in different samples treated at different temperature measured by XPS.

Sample	1.5PtL-SBA-15	1.5Pt-SBA-15-400	1.5Pt-SBA-15-500

Relative N content (%)	100	95	50



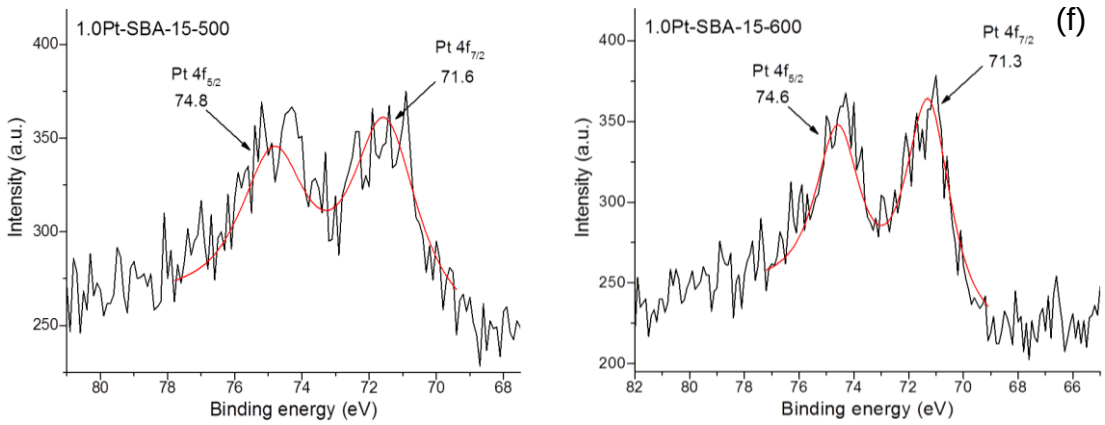


Fig. S2 XPS spectra of (a) 0.2Pt-SBA-15-500, (b) 0.2Pt-SBA-15-600, (c) 0.3Pt-SBA-15-500, (d) 0.3Pt-SBA-15-600, (e) 1.0Pt-SBA-15-500, (f) 1.0Pt-SBA-15-600.

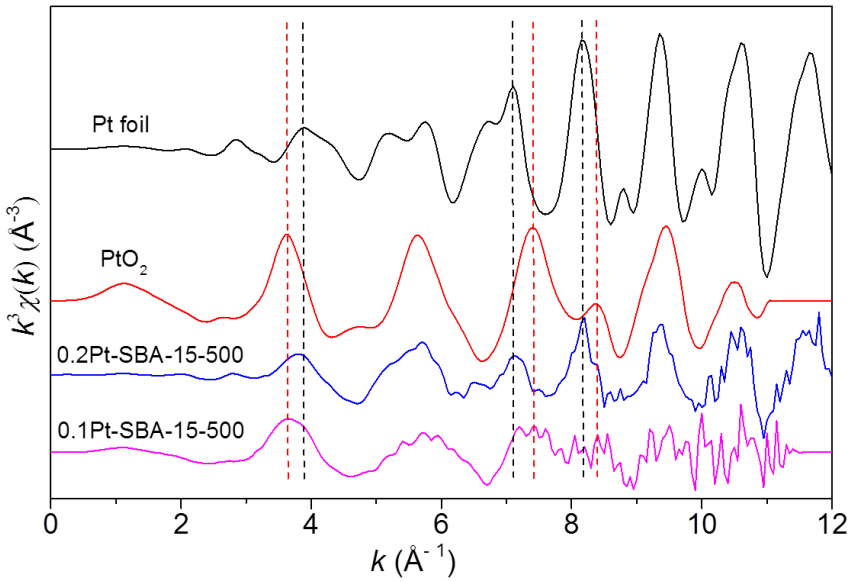
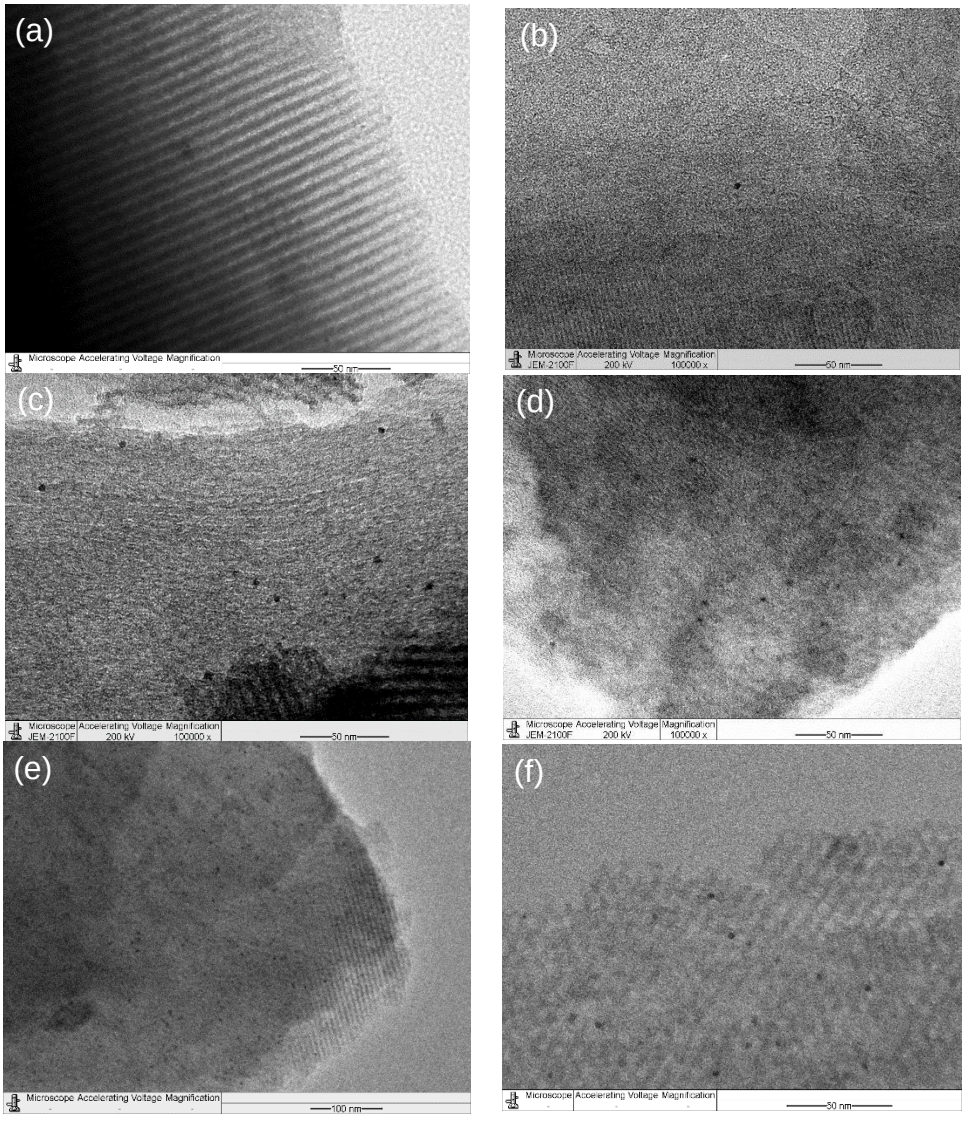


Fig. S3 k^3-weighted k-space spectra at the Pt L_3-edge for different Pt samples. Black dashed lines refer to the phase for Pt–Pt contribution and red dashed lines refer to the phase for Pt–O contribution.


(a)
Microscope Accelerating Voltage Magnification
50 nm
(b)
Microscope Accelerating Voltage Magnification
JEM-2100F 200 kV 100000 x
50 nm
(c)
Microscope Accelerating Voltage Magnification
JEM-2100F 200 kV 100000 x
50 nm
(d)
Microscope Accelerating Voltage Magnification
JEM-2100F 200 kV 100000 x
50 nm
(e)
Microscope Accelerating Voltage Magnification
100 nm
(f)
Microscope Accelerating Voltage Magnification
50 nm

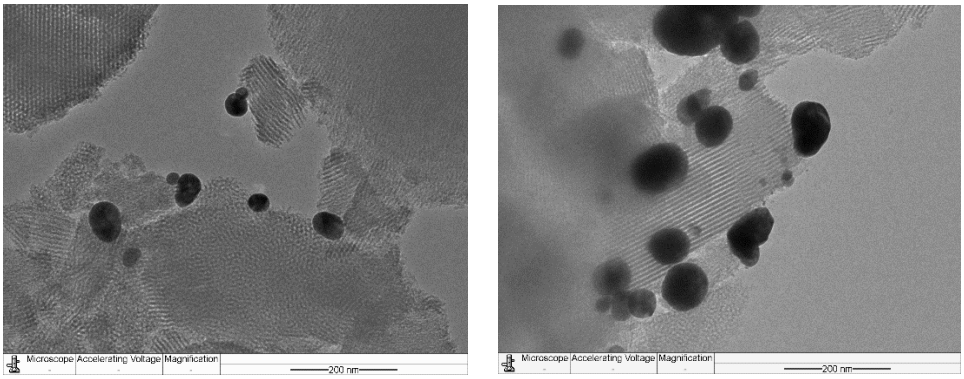


Fig. S4 TEM images of (a, b) 0.2Pt-SBA-15-600, (c, d) 0.3Pt-SBA-15-500, (e, f) 1.0Pt-SBA-15-500, (g) 0.3Pt-SBA-15-500-C, (h) 1.0Pt-SBA-15-500-C.

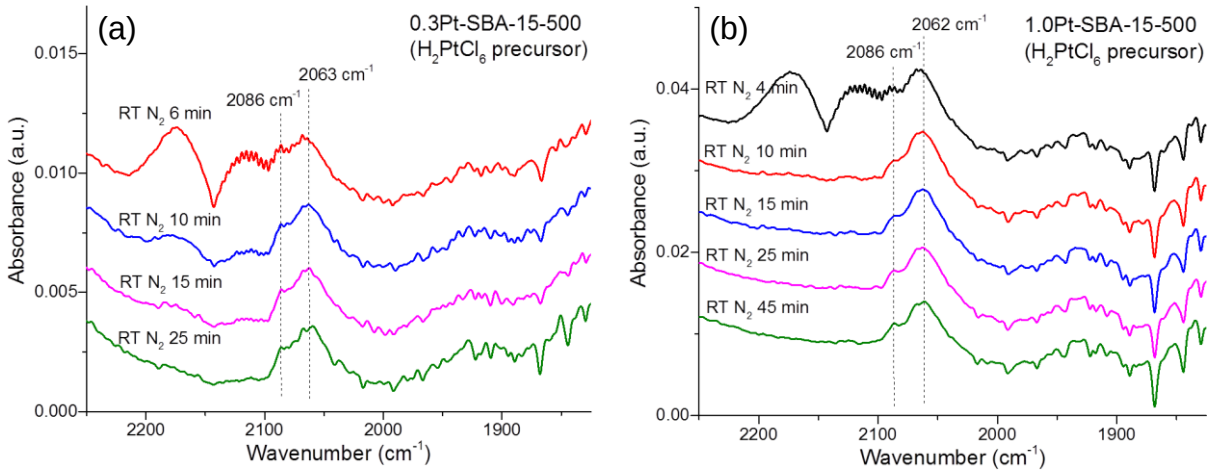
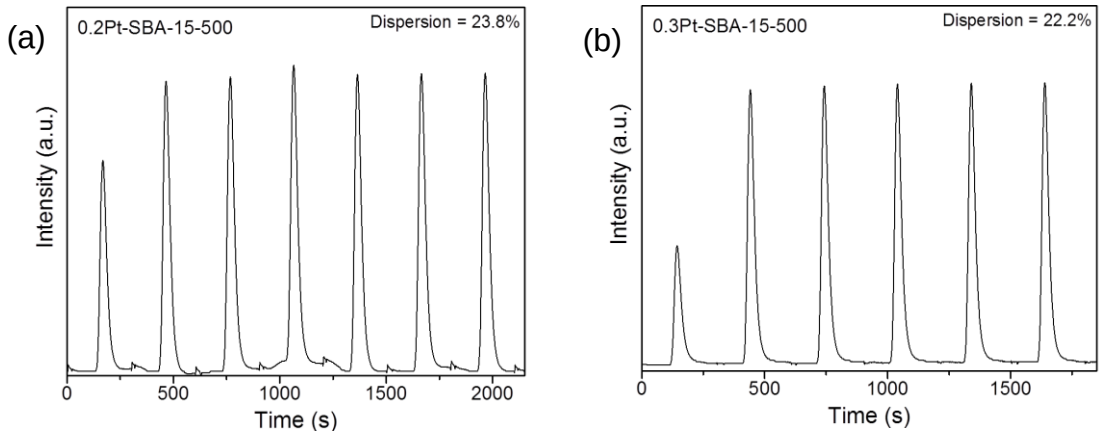


Fig. S5 IR spectra of CO adsorbed on different samples: (a) 0.3Pt-SBA-15-500-C, (b) 1.0Pt-SBA-15-500-C.



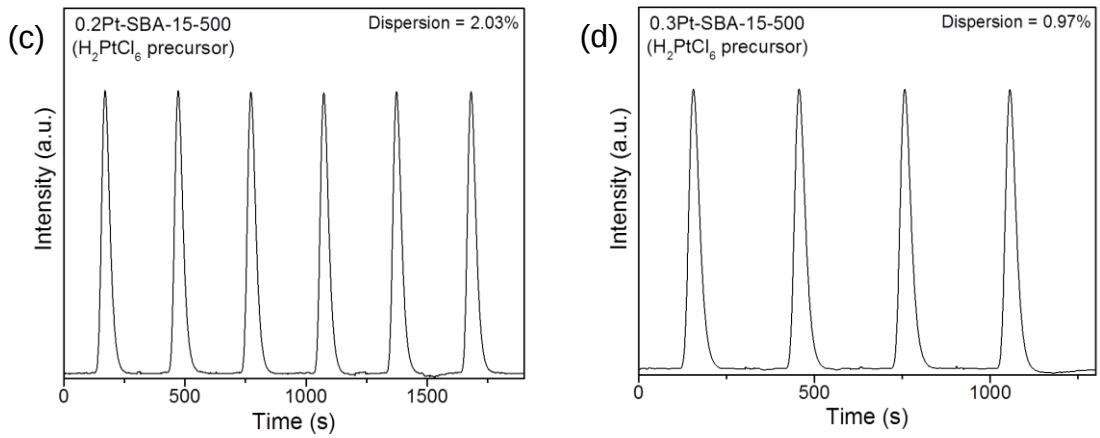


Fig. S6 H_2 pulse titration profiles of samples after treatment with air: (a) 0.2Pt-SBA-15-500, (b) 0.3Pt-SBA-15-500, (c) 0.2Pt-SBA-15-500-C, (b) 0.3Pt-SBA-15-500-C.

Table S3 Elemental analysis results of [Pt(^{t}Bu$_3$tpy)Cl]Cl·H_2O complex.

Element	C	H	N
Calculated (wt%)	47.30	5.44	6.13
Found (wt%)	47.07	5.28	6.07

Table S4 Selective hydrogenation of phenylacetylene (PhAc).[a]

Entry	**Catalyst**	**PhAc/Pt**	***t* (min)**	**Conv. (%)**	**$S_{Styrene}$ (%)**	**$S_{Ethylbenzene}$ (%)**	**Specific activity (mol_{sub}/mol_{Pt} h)**
1	0.2Pt-SBA-15-500	4000	15	24.3	94.1	5.9	3888
2	0.3Pt-SBA-15-500	4000	15	30.6	92.5	7.5	4896
3	0.2Pt-SBA-15-500	4000	60	64.8	89.4	10.6	
4	0.3Pt-SBA-15-500	4000	60	87.2	86.1	13.9	
5	1.0Pt-SBA-15-500	4000	60	99.6	67.6	32.4	
6	0.3Pt-SBA-15-500-C	4000	60	28.3	89.5	10.5	1132
7	1.0Pt-SBA-15-500-C	4000	60	24.3	94.2	5.8	972
8	0.2Pt-SBA-15-500-C	1000	120	63.0	85.7	14.3	
9	0.3Pt-SBA-15-500-C	1000	120	86.3	77.9	22.1	
10	1.0Pt-SBA-15-500-C	1000	120	35.4	82.5	17.5	

[a]Reaction condition: phenylacetylene = 18.9 mg (0.1845 mmol), 2 mL methanol, 10 bar H_2, room temp.

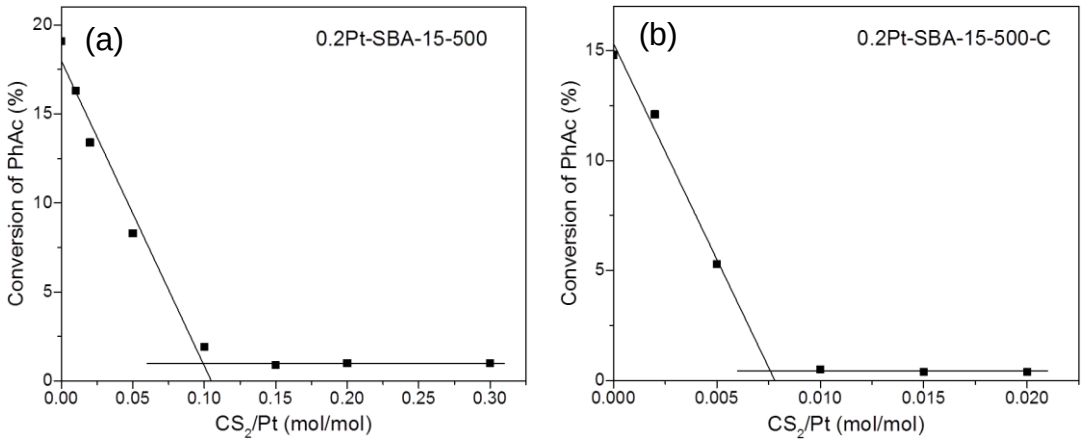
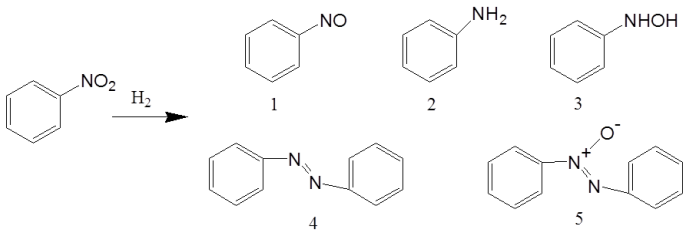


Fig. S7 Conversion of phenylacetylene over (a) 0.2Pt-SBA-15-500 and (b) 0.2Pt-SBA-15-500-C as a function of CS_2/Pt. Reaction conditions: (a) PhAc/Pt = 4000, solvent = methanol (2 mL), 10 bar H_2, room temperature, t = 15 min; (b) PhAc/Pt = 1000, solvent = methanol (2 mL), 10 bar H_2, room temperature, t = 30 min. In each case, 5 mg of catalyst was poisoned with certain amount of CS_2 dissolved in methanol prior to the addition of phenylacetylene.

From the fitting curves, by assuming one CS_2 molecule blocking two active sites, the active sites fractions of 0.2Pt-SBA-15-500 and 0.2Pt-SBA-15-500-C catalysts were 20% and 1.5%, respectively.

Table S5 Hydrogenation of nitrobenzene (NB).[a]



Entry	Catalyst	NB/Pt	H_2 (bar)	*t* (min)	Conv (%)	Sel 1 (%)	Sel 2 (%)	Sel 3 (%)	Sel 4 (%)	Sel 5 (%)
1	0.2Pt-SBA-15-500	4000	10	15	100	24.4	47.2	0	0	28.4
2	0.2Pt-SBA-15-500	4000	10	60	100	15.7	58.3	0	0.7	25.3
3	0.2Pt-SBA-15-450	4000	10	15	6.4	0	100	0	0	0
4	0.2Pt-SBA-15-450	2000	10	15	100	19.9	64.1	0	0	16.0
5	0.2Pt-SBA-15-500	8000	10	15	68.2	32.2	61.8	0	0	6.0
6	0.2Pt-SBA-15-500 (10 °C)	4000	10	15	16.4	0	100	0	0	0
7	0.2Pt-SBA-15-500 (60 °C)	4000	10	15	100	15.1	79.5	0	0	5.4
8	0.2Pt-SBA-15-500	4000	10	10	100	39.5	45.4	0	0	15.1
9	0.2Pt-SBA-15-500	4000	2	15	100	32.0	59.9	0	0	8.1
10	0.2Pt-SBA-15-500	4000	5	15	100	35.4	58.1	0	0	6.5
11	0.2Pt-SBA-15-500	4000	20	15	100	38.7	53.9	0	0	7.4
12	0.2Pt-SBA-15-500 (EA 50)	4000	10	15	76.1	7.7	33.9	0	0	58.4
13	0.2Pt-SBA-15-500 (EA 50)	4000	2	30	3.0	0	0	0	0	100
14	0.2Pt-SBA-15-500 (EA 50)	4000	5	30	36.5	5.6	28.7	0	0	65.7
15	0.2Pt-SBA-15-500 (EA 50)	4000	5	60	100	7.9	25.6	0	0	66.5
16	0.2Pt-SBA-15-500-C	4000	10	15	0	0	0	0	0	0
17	0.2Pt-SBA-15-500-C	4000	10	60	5.2	0	100	0	0	0
18	0.2Pt-SBA-15-500-C	2000	10	60	19.0	0	100	0	0	0

[a]Reaction condition: NB = 22.7 mg (0.1845 mmol), 2 mL methanol, room temp. EA: ethanolamine (50 μL).

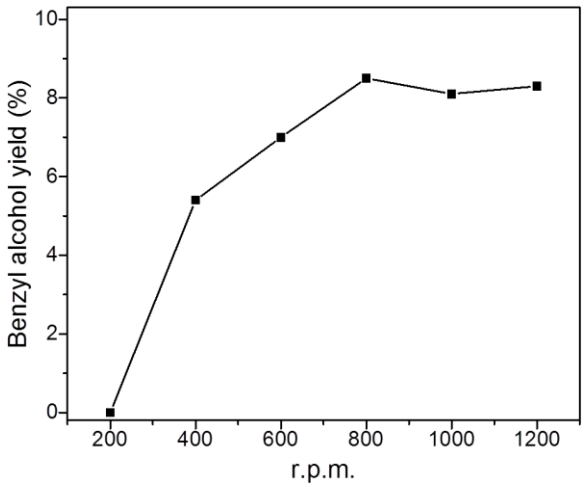


Fig. S8 Benzyl alcohol yield against rotation per minute (r.p.m.) using 0.2Pt-SBA-15-500 catalyst. Reaction conditions: catalyst = 12 mg, benzaldehyde = 6.2 μL, benzaldehyde/Pt = 500, solvent = methanol (2 mL), H_2 pressure = 10 bar, room temperature, *t* = 30 min.

Table S6 Hydrogenation of benzaldehyde (BZ).

Entry	**Catalyst**	**BZ/Pt**	***T*** **(°C)**	**H_2 (bar)**	***t*** **(min)**	**Benzyl alcohol yield (%)**	**Specific activity (mol_{sub}/mol_{Pt} h)**
1	0.2Pt-SBA-15-500	1000	50	20	60	46.8	468
2	0.2Pt-SBA-15-500	1000	50	10	60	60.4	604
3	0.2Pt-SBA-15-500	500	50	10	60	78.2	391
4	0.2Pt-SBA-15-500-C	250	60	10	120	22.1	28
5	0.2Pt-SBA-15-500-C	250	50	20	120	12.9	16

Solvent: methanol (2 mL)

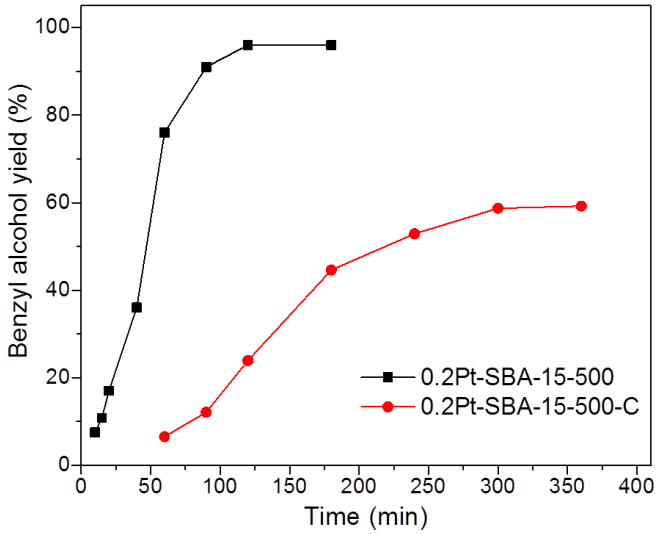


Fig. S9 Benzyl alcohol yield at different time using both 0.2Pt-SBA-15-500 and 0.2Pt-SBA-15-500-C catalysts. Reaction conditions: BZ/Pt = 500 for 0.2Pt-SBA-15-500 and 1:250 for 0.2Pt-SBA-15-500-C, solvent = methanol (2 mL), H_2 pressure = 10 bar, T = 50 °C.

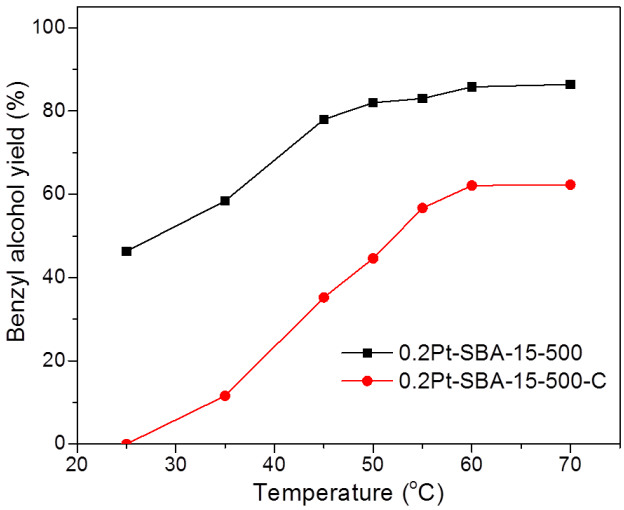


Fig. S10 Benzyl alcohol yield at different temperature using both 0.2Pt-SBA-15-500 and 0.2Pt-SBA-15-500-C catalysts. Reaction conditions: BZ/Pt = 500 for 0.2Pt-SBA-15-500 and 1:250 for 0.2Pt-SBA-15-500-C, solvent = methanol (2 mL), H_2 pressure = 10 bar, room temperature, t = 1 h for 0.2Pt-SBA-15-500 and 3 h for 0.2Pt-SBA-15-500-C.

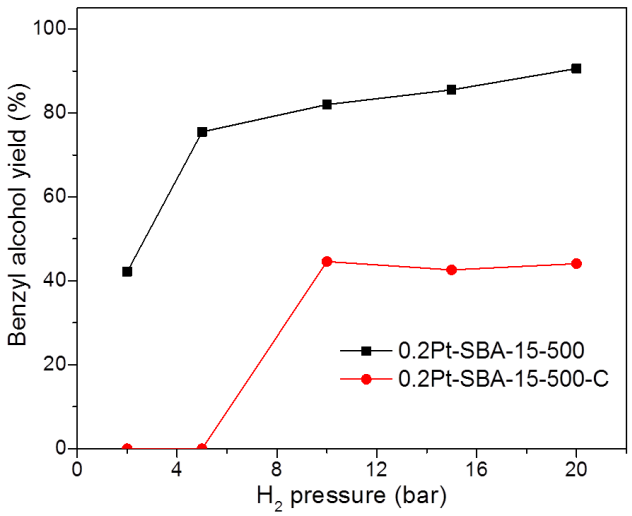


Fig. S11 Benzyl alcohol yield at different H_2 pressure using both 0.2Pt-SBA-15-500 and 0.2Pt-SBA-15-500-C catalysts. Reaction conditions: BZ/Pt = 500 for 0.2Pt-SBA-15-500 and 1:250 for 0.2Pt-SBA-15-500-C, solvent = methanol (2 mL), *T* = 50 °C, *t* = 1 h for 0.2Pt-SBA-15-500 and 3 h for 0.2Pt-SBA-15-500-C.

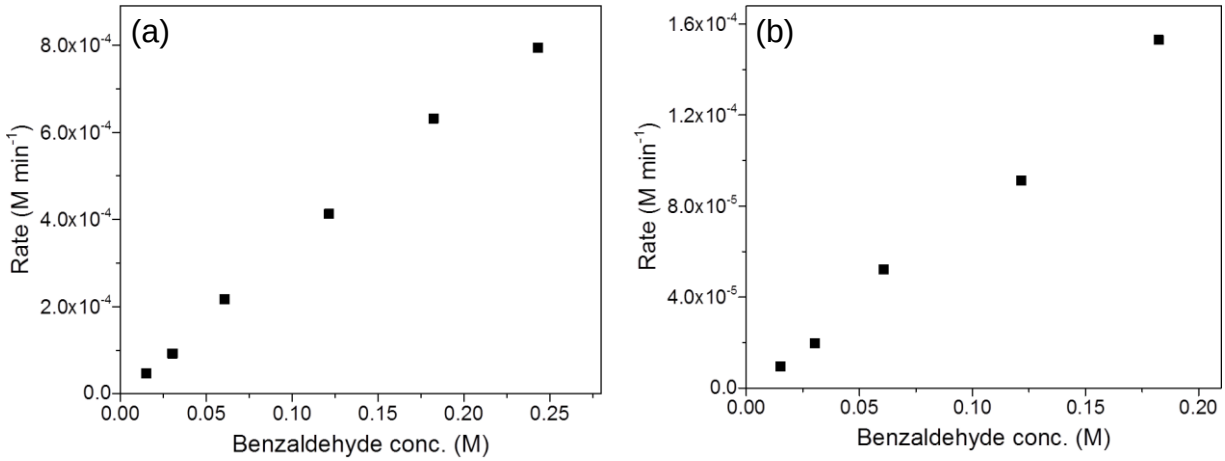


Fig. S12 Reaction rate *vs.* benzaldehyde concentration. Reaction conditions: catalyst = 12 mg (for 0.2Pt-SBA-15-500) and 24 mg (for 0.2Pt-SBA-15-500-C), solvent = methanol (2 mL), H_2 pressure = 10 bar, *t* = 30 min (for 0.2Pt-SBA-15-500) and 3 h (for 0.2Pt-SBA-15-500-C), *T* = room temperature (for 0.2Pt-SBA-15-500) and 35 °C (for 0.2Pt-SBA-15-500-C).

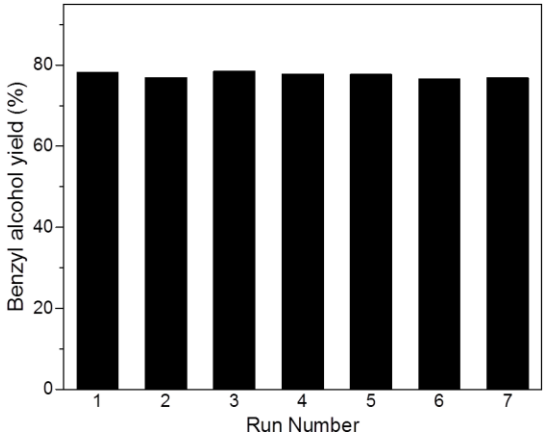


Fig. S13 Recycling test of 0.2Pt-SBA-15-500 catalyst for the hydrogenation of benzaldehyde. Reaction conditions: BZ/Pt = 500, solvent = methanol (2 mL), H_2 pressure = 10 bar, T = 50 °C, t = 1 h.

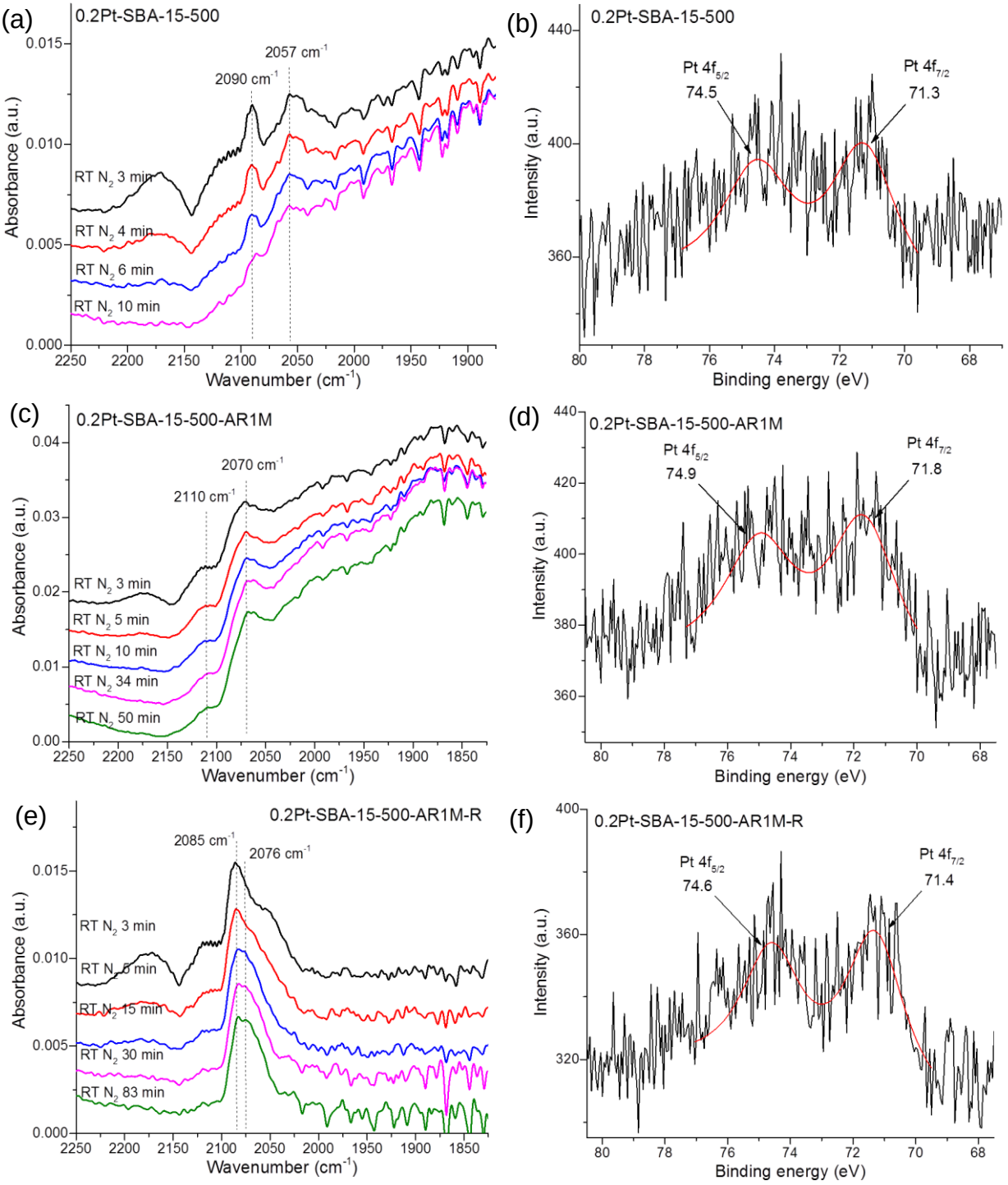


Fig. S14 IR spectra of CO adsorbed on different 0.2Pt-SBA-15-500 samples (a) before aqua regia treatment, (c) after aqua regia treatment, (e) after H_2 reduction of aqua regia treated sample, and their corresponding X-ray photoelectron spectra (b, d and f respectively).

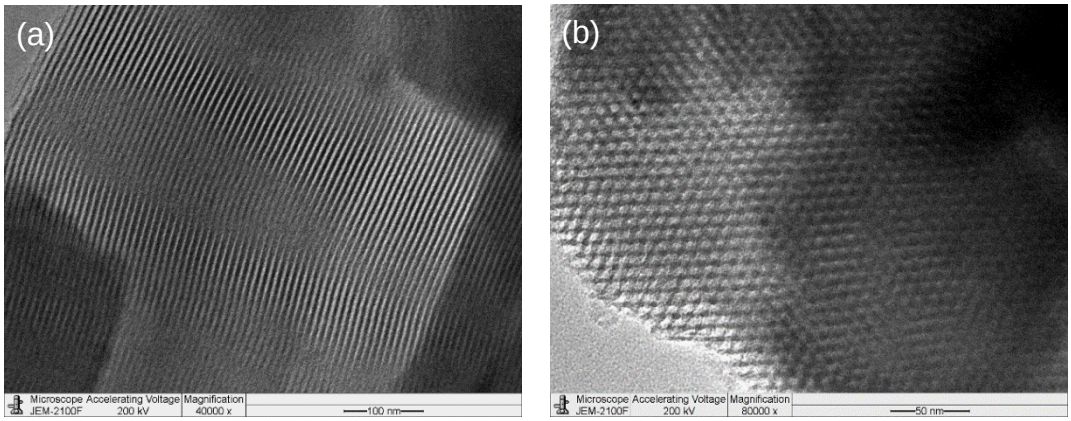


Fig. S15 TEM images of 0.2Pt-SBA-15-500 after the treatment with 1 M aqua regia.

Table S7 Hydrogenation of benzaldehyde (BZ) using 0.2Pt-SBA-15-500 catalysts before and after the treatment with aqua regia.

Entry	Catalyst	Treatment	Benzyl alcohol yield (%)	Specific activity (mol_{sub}/mol_{Pt} h)
1	0.2Pt-SBA-15-500	-	31.4	157
2	0.2Pt-SBA-15-500	1 M AR	13.8	69
3	0.2Pt-SBA-15-500	1 M AR / H_2	25.2	126
Reaction conditions: BZ/Pt = 500, 2 mL methanol, 10 bar H_2, RT, 1 h.				

Table S8 Hydrogenation of phenylacetylene (PhAc) using 0.2Pt-SBA-15-500 catalysts before and after the treatment with aqua regia.

Entry	Catalyst	Treatment	PhAc conversion (%)	Specific activity (mol_{sub}/mol_{Pt} h)	$S_{styrene}$ (%)	$S_{ethylbenzene}$ (%)
1	0.2Pt-SBA-15-500	-	11.2	3584	86.1	13.9
2	0.2Pt-SBA-15-500	1 M AR	7.8	2496	95.5	4.5
3	0.2Pt-SBA-15-500	1 M AR / H_2	10.7	3424	94.2	5.8
Reaction conditions: PhAc/Pt = 8000, 2 mL methanol, 10 bar H_2, RT, 15 min.						