Supplementary Information for

Selective Hydrodeoxygenation of Aromatics to Phenols by La Single Atoms Modified Pt Nanoparticles Supported on Al_2O_3

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This supporting information contains

Materials and Methods

Chemicals and materials

γ-Al_2O_3 (99.9%), α-Al_2O_3 (99.9%), La_2O_3 (99.9%), ZrO_2 (99.9%), MgO (99.9%) and TiO_2 (99.9%) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. 1,2-Dihydroxybenzene (98%), $LaCl_3$ (99.9%) and MoO_3 (99.9%) were obtained from Anhui Senrise Technologies Co., Ltd. MCM-41 (All-silicon, hydrogen type) and ZSM-5 (All-silicon, hydrogen type) zeolites were purchased from Nanjing XFNANO Materials Tech. Co., Ltd. Guaiacol (98.0%) and anisole (98.0%), 3-butoxyphenol (96.0 %), vanillin (98.0%), phenyl ether (99.0%) and benzyl phenyl ether (98.0%) were purchased from TCI (Shanghai) Development Co., Ltd. All the chemicals were used without further purification.

Catalyst synthesis

Synthesis of La-modified Al_2O_3 supports. Typically, a certain amount of $LaCl_3$ aqueous solution was slowly dropped into γ-Al_2O_3 (1.0 g) under magnetic stirring. Then, the mixed liquid was stirred at room temperature for 4 h, followed by rotary evaporation of the liquid under 60 °C. The as-synthesized solid was dried overnight at 60 °C in a convection oven, followed by calcination at 400 °C for 3 h under air atmosphere. These La-modified supports were denoted as Lax-Al_2O_3, where x represents the loading amount of La (La to γ-Al_2O_3 in the mass ratio, see Table S1).

Synthesis of Pt/La_x-Al_2O_3 catalysts. The Pt/La_x-Al_2O_3 catalyst was prepared by incipient wetness method. Typically, a certain amount of H_2PtCl_6 (1 mg/mL) aqueous solution was slowly dropped into La_x-Al_2O_3 support and magnetically stirred for 24 h. Then the water was evaporated at 60 °C under vacuum. The obtained solid was reduced at 300 °C for 2 h under a flowing H_2 atmosphere.

Synthesis of M/C catalysts. The synthesis methods of Pd/C, Pt/C, Ni/C (1 wt% Pd, Pt and Ni) catalysts was similar to Pt/La-Al_2O_3 catalysts, except for the support becoming carbon (Ketigenblack ECP60JD). Typically, the same molar amount of $PdCl_2$, $H_2PtCl_6 \cdot 6H_2O$ and $NiCl_2 \cdot 6H_2O$ were slowly dropped into carbon support and magnetically stirred for 24 h. Then the water was evaporated at 60 °C under vacuum. The reduction temperatures of the Pd/C, Pt/C and Ni/C catalysts were 200 °C, 300 °C and 450 °C, respectively.

Catalytic reaction

The hydrogenation of guaiacol was carried out in a Teflon-lined stainless-steel reactor of 20 mL with a magnetic stirrer. In a typical experiment, a suitable amount of reactant, catalyst, and water were loaded into the reactor. The reactor was sealed and purged with N_2 for three times to remove the air at room temperature and subsequently charged with desired gas. Then the reactor was placed in a furnace at desired reaction temperature. When the reactor reached the desired reaction temperature, the stirrer was started with a stirring speed of 800 rpm, and the reaction time was recorded. After the reaction, the reactor was placed in ice water, and the gas was released, passing through the ethyl acetate. The reaction mixture in the reactor

was transferred into a centrifuge tube. Then the reactor was washed with the ethyl acetate used for the gas filtration, which was finally combined with the reaction mixture. After centrifugation, the catalyst was separated from the reaction mixture. The quantitative analysis of the liquid products in the organic phase was conducted using a GC (Shimazdu 2010 Plus) equipped with a flame ionization detector (FID) and HP-5MS capillary columns (0.25 mm in diameter, 30 m in length). Identification of the products and reactant was performed using a GC-MS [Agilent 8890, HP-5MS capillary column (0.25 mm in diameter, 30 m in length)] and by comparing the retention time to respective standards in GC traces. Decane was used as the internal standard to determine the conversions of substrates, selectivities and yields of the products. In addition, identification of the isolated products in the reaction liquid was also conducted by 1H analyses on a Bruker Avance III 400 HD with Chloroform-d as the solvent. The carbon balances for the reactions were calculated using C6-membered ring balance which was given relative to the 6-membered ring products. The C6-membered ring balances for the reaction of the substrates were better than 99%. For the calculations of turnover frequency (TOF), turnover number (TON) and reaction rate, every metal atom was assumed to be the potential active site, which is a reasonable and commonly used lower bound for the calculations.

$$TON\ of\ guaiacol = \frac{Phenol\ produced\ (mol)}{Active\ mental\ (mol)} \times 100\% \qquad \text{eq. (S1)}$$

Characterization

X-ray diffraction (XRD) patterns were collected on a Rigaku Ultima IV X-ray diffractometer using Cu Kα radiation at 35 kV and 25 mA (λ = 1.5405 Å) over a 2θ ranging from 5 °C to 90 °C at a scanning speed of 5°/min. The morphology and size of the supports and catalysts were studied by scanning electron microscopy (SEM) on a Hitachi S-4800 microscope and transmission electron microscopy (TEM) on a JEOL JEM-2100 microscope at an accelerating voltage of 200 kV. The high angle annular dark-field scanning TEM (HAADF-STEM) was operated at 300 kV by a JEOL Grand ARM 300F. The Pt and La content were quantified by inductively coupled plasma emission spectrometer (ICP-OES) on Optima 8300. X-ray photoelectron spectroscopy (XPS) experiments were carried out with $Al_{k\alpha}$ (hv = 1486.36 eV) radiation using a Thermo Scientific K-Alpha spectrometer. Hydrogen Temperature-Programmed Reduction (H_2-TPR) and H_2 temperature programmed desorption (H_2-TPD) experiments were conducted on a Micromeritics AutoChem II Chemisorption Analyzer. The specific experiment of H_2-TPR is as follows: the sample of 50 mg was put into a tube reactor of quartz followed by a pretreatment at 200 °C for 1 h in a He stream and then cooling to 50 °C. Then, it was heated from 50 to 800 °C at a ramping rate of 10 °C min^{-1} in a flow of 10 % H_2/N_2. At the same time, the thermal conductivity detector (TCD) signals were recorded to get the H_2-TPR profiles. Typically, the experimental procedure for H_2-TCD is conducted as follows: the sample of 50 mg was put into a tube reactor of quartz followed by a pretreatment at 200 °C for 1 h in a H_2-Ar stream and then cooling to 50 °C. The gas flow was

changed to Ar and maintain for 1 h. After the baseline was stable, it was heated from 50 to 800 °C at a ramping rate of 10 °C min^{-1}, and the TCD signals were recorded to get the H_2-TPD profiles. Dispersion was measured by CO pulse chemisorption. Typically, a sample (100 mg) was first pretreated under H_2 at a flow rate of 30 $cm^3 \cdot min^{-1}$ and heated to 300 °C at a heating rate of 10 $K \cdot min^{-1}$. Cooling to 50 °C was carried out under helium at a rate of 30 $cm^3 \cdot min^{-1}$. The dispersion was then measured by CO pulse chemisorption at room temperature. The flow rate of helium during the chemisorption measurement was 10 $cm^3 \cdot min^{-1}$. Metal dispersion was calculated by assuming a CO/surface Pt atom ratio of 1:1.[1]

***In-situ* DRIFT measurements**

In situ diffuse reflection infrared Fourier transform (DRIFT) spectra of the transformation of the lignin model compound were recorded with a NICOLET iS50 FT-IR spectrometer (Thermo Scientific, USA) equipped with a Harrick cell with a mercury cadmium telluride (MCT-A) detector cooled through liquid nitrogen. The spectra were acquired in transmission mode between 4000 and 1000 cm^{-1}. Prior to the measurements, the catalyst sample was pretreated by heating it from room temperature to 200 °C for 1 h under a N_2 flow of 10 mL/min. Then, the sample was cooled to room temperature and the background spectrum was recorded. Subsequently, 10 μL of the solution (1 mg of substarte, 10 μL of MeOH) was introduced to the sample, and the cell was purged with H_2 and sealed at 0.1 MPa H_2 in the end. Finally, the in-situ DRIFT spectra of the hydrogenolysis reaction at different temperatures and times were recorded. In addition, the in-situ DRIFT of Pt/$La_{0.1}$-Al_2O_3 for the adsorption of phenol and catechol were recorded under different temperatures using the same experimental method.

Stability study

The recyclability of Pt/$La_{0.1}$-Al_2O_3 catalyst was tested using the reaction of guaiacol. After the reaction, the reaction mixture in the reactor was transferred into a centrifuge tube. Then the reactor was washed with ethyl acetate, which was combined with the reaction mixture. Subsequently, the reaction mixture was centrifuged and the ethyl acetate layer was analyzed by GC. After that, the used Pt/$La_{0.1}$-Al_2O_3 catalyst was separated from the reaction mixture and successively washed with ethanol (5 × 10 mL) and water (5 × 10 ml). Then, the recovered catalyst was reused directly for the next run. To study the stability of Pt and La atoms, hot filtration leaching test was also adopted during another recyclability experiments of the Pt/La-Al_2O_3 catalyst to determine the leaching of Pt.[2] After 6 h in the 5th run, the reaction mixture was hot filtered under vacuum, and the catalyst was separated. Then, the liquid phase was analyzed by ICP-OES.

Kinetic study

The reaction order was determined by the initial rate method. Typically, a series of guaiacol solutions with varying initial guaiacol concentrations (0.125, 0.25, 0.375, 0.5 mmol/mL), under an H_2 pressure of 0.1 MPa, 200 °C, in a Teflon-lined stainless-steel reactor of 20 mL. Record the time when the temperature reaches 200 °C as t = 0, and

collect small sample at t= 0, 5, 10, 15, 20 min using a syringe. Identification of the products and reactant was performed using a GC. The rate law for the guaiacol HDO reaction is assumed to be:

$$r = k \cdot {c_G}^{n_1} \cdot {c_{H_2}}^{n_2} \qquad \text{eq. (S2)}$$

Where k is the kinetic rate constant, c_G is the guaiacol concentration, c_{H_2} is the initial H_2 pressure, n_1 is the reaction order with the respect to guaiacol, and n_2 is the order with respect to H_2.

Kinetic experiments for the hydrodeoxygenation of guaiacol were conducted at 160, 180, 200 and 220 °C, with 20 mg catalyst, under 0.1 MPa H_2 pressure, in a Teflon-lined stainless-steel reactor of 20 mL. In the kinetic analysis, the reaction is assumed constant to be power law reaction and the hydrogen solubility is assumed the constant.[3] In this work, the HDO of guaiacol is determined to be the first-order kinetics (θ=1) with respect to the corresponding reactant.[4] Based on Arrhenius equation, the reaction rate is denoted as

$$-\frac{dc(guaiacol)}{dt} = kc(guaiacol)^{\theta} \qquad \text{Eq. (S3)}$$

$$\ln\frac{c_t}{c_0} = -kt \qquad \text{Eq. (S4)}$$

$$\ln k = \ln A - \frac{Ea}{RT} \qquad \text{Eq. (S5)}$$

where k represents the kinetic rate constant, c_0 is the initial guaiacol concentration, c_t is the guaiacol concentration at the reaction time, R = 8.314 $J \cdot mol^{-1} \cdot K^{-1}$, A is pre-exponential factor, T is the dynamic temperature, Ea is the apparent activation energy and reaction order θ = 1.

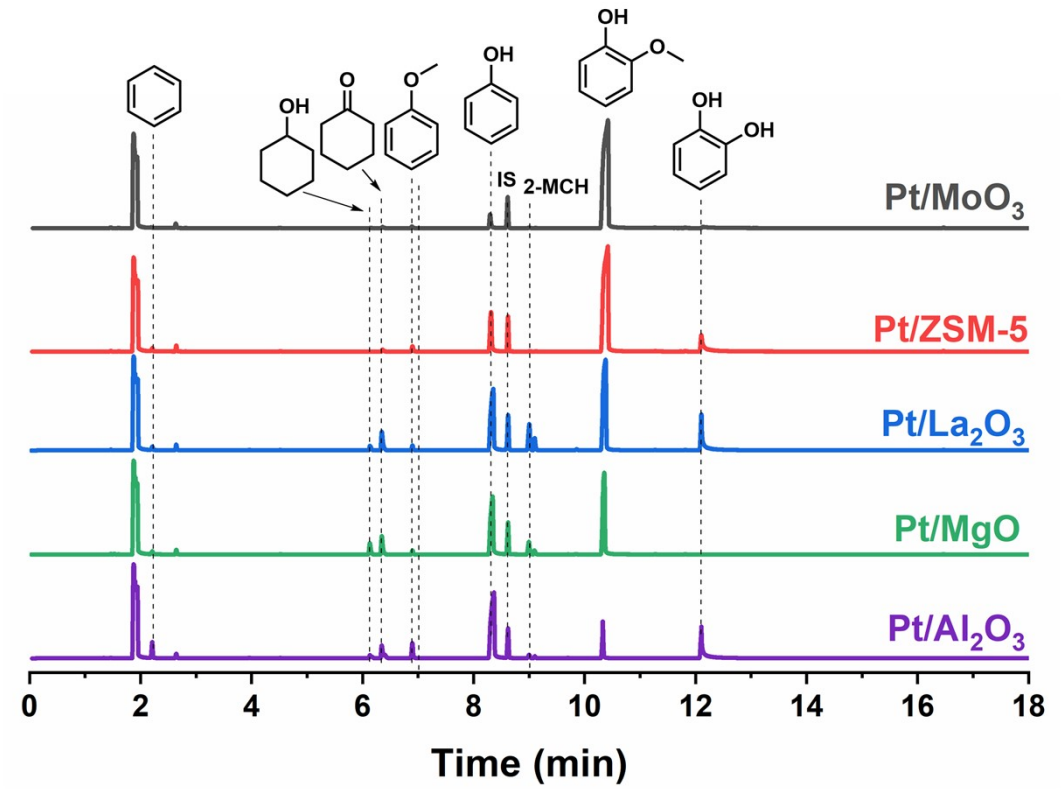


Figure S1. GC trace of the liquid mixture. Reaction conditions: guaiacol (0.5 mmol), Pt catalysts (0.02 g), H_2O (2.0 mL), 200 °C, 4.0 h, 0.1 MPa H_2, 800 rpm.

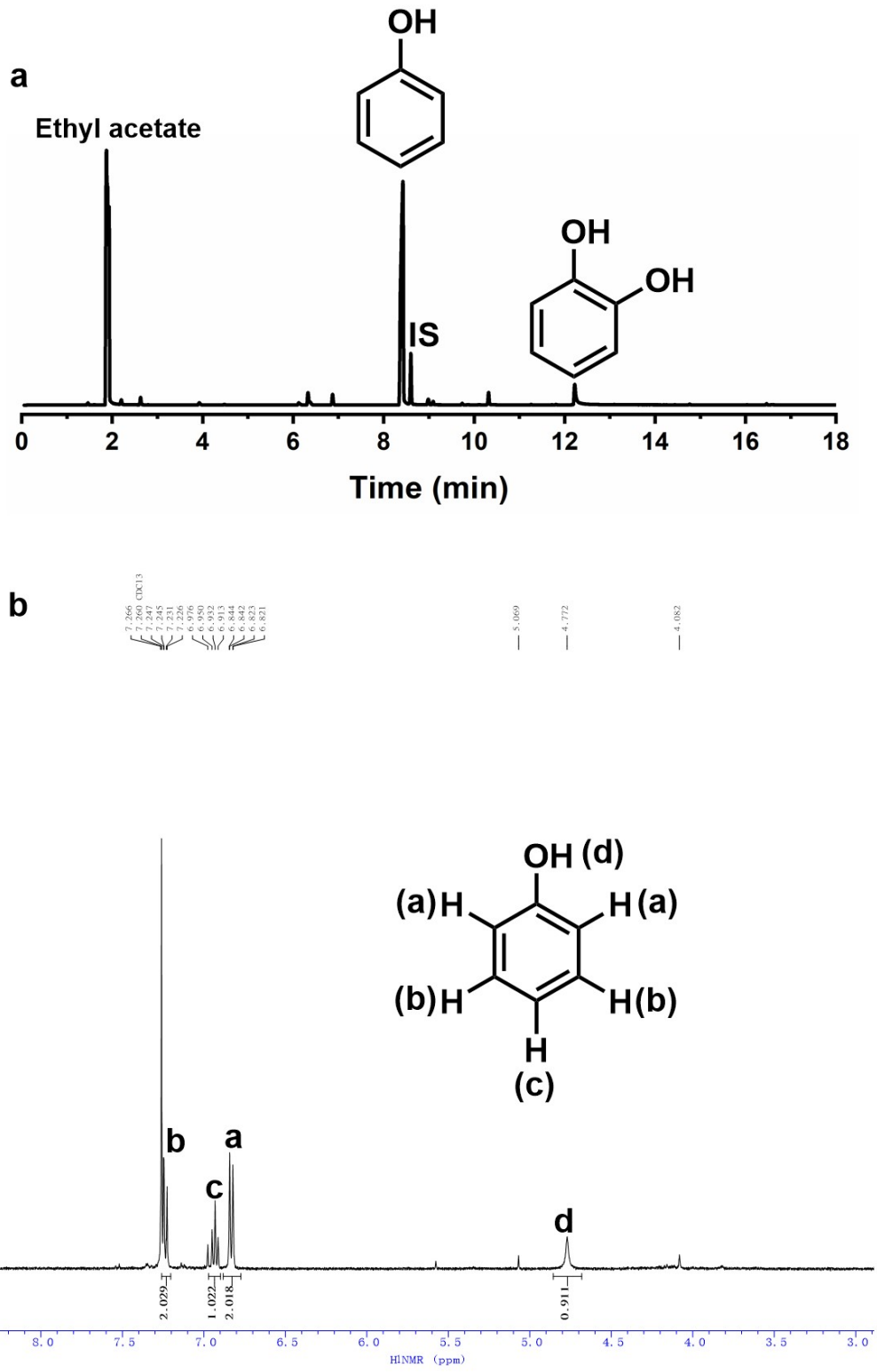


Figure S2. (a) GC trace of the liquid mixture. (b) 1H NMR of the liquid which was extracted by Chloroform-d. Reaction conditions: guaiacol (0.5 mmol), Pt/$La_{0.1}$-Al_2O_3 (0.02 g), H_2O (2.0 mL), 200 °C, 6.0 h, 0.1 MPa H_2, 800 rpm.

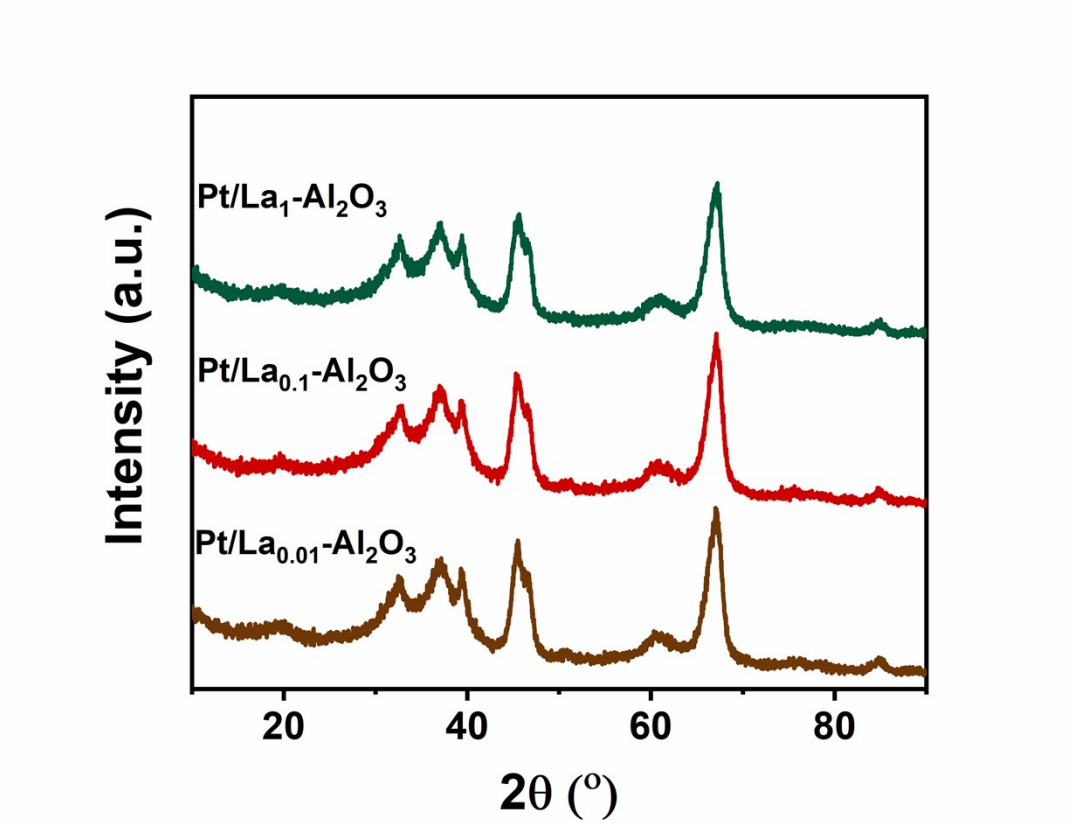


Figure S3. XRD patterns of Pt/La$_x$-Al$_2$O$_3$ catalysts.

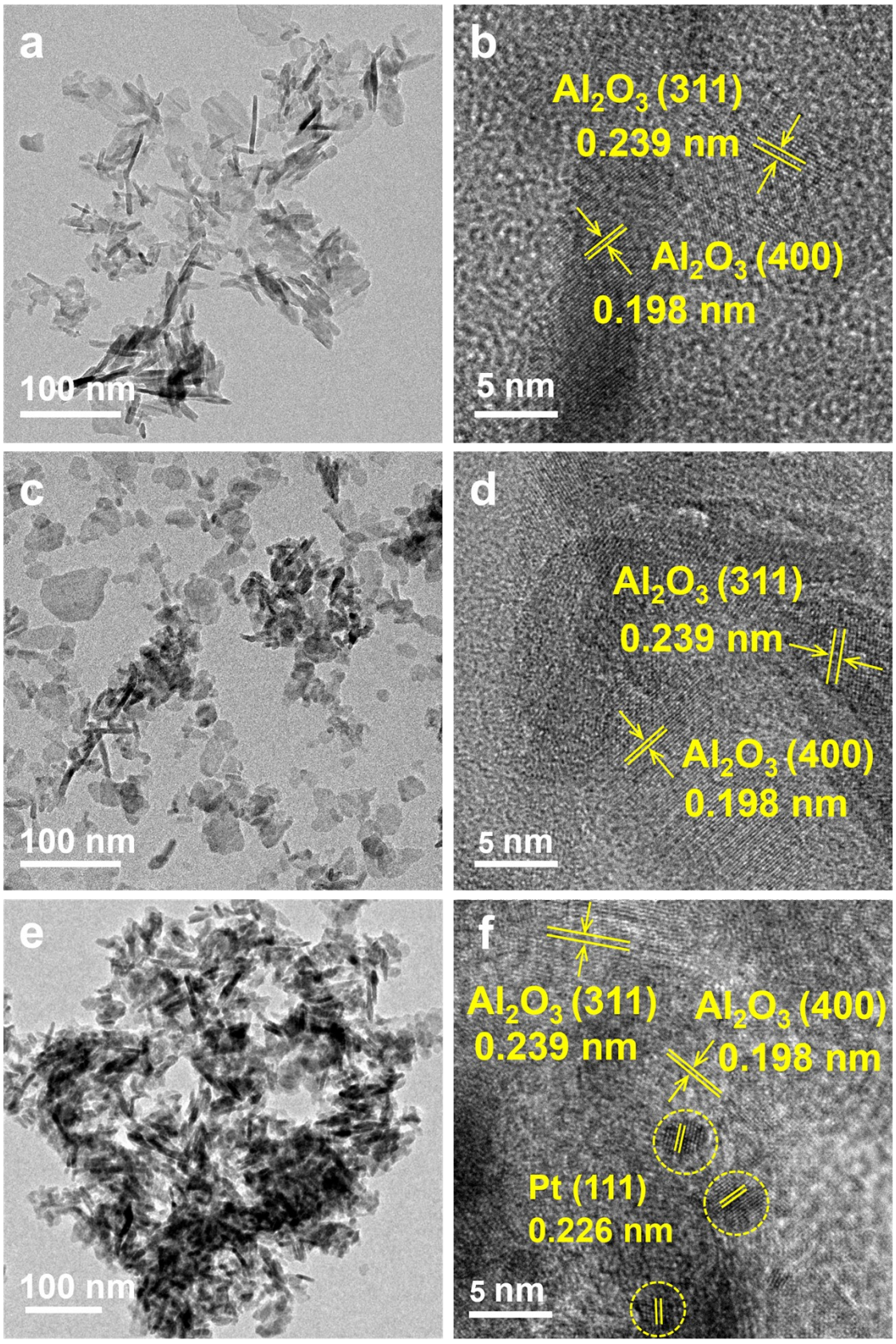


Figure S4. TEM analysis. (a) and (b) Al_2O_3. (c) and (d) $La_{0.1}$-Al_2O_3. (e) and (f) Pt/Al_2O_3, where marked yellow circles represent Pt NPs.

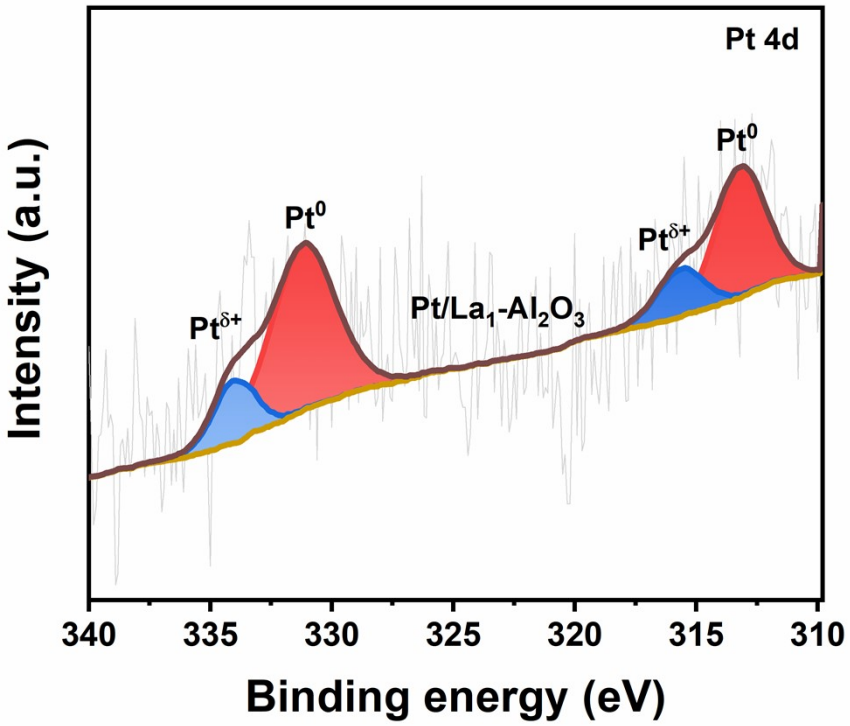


Figure S5. XPS spectrum of Pt 4d for Pt/La_1-Al_2O_3 catalyst.

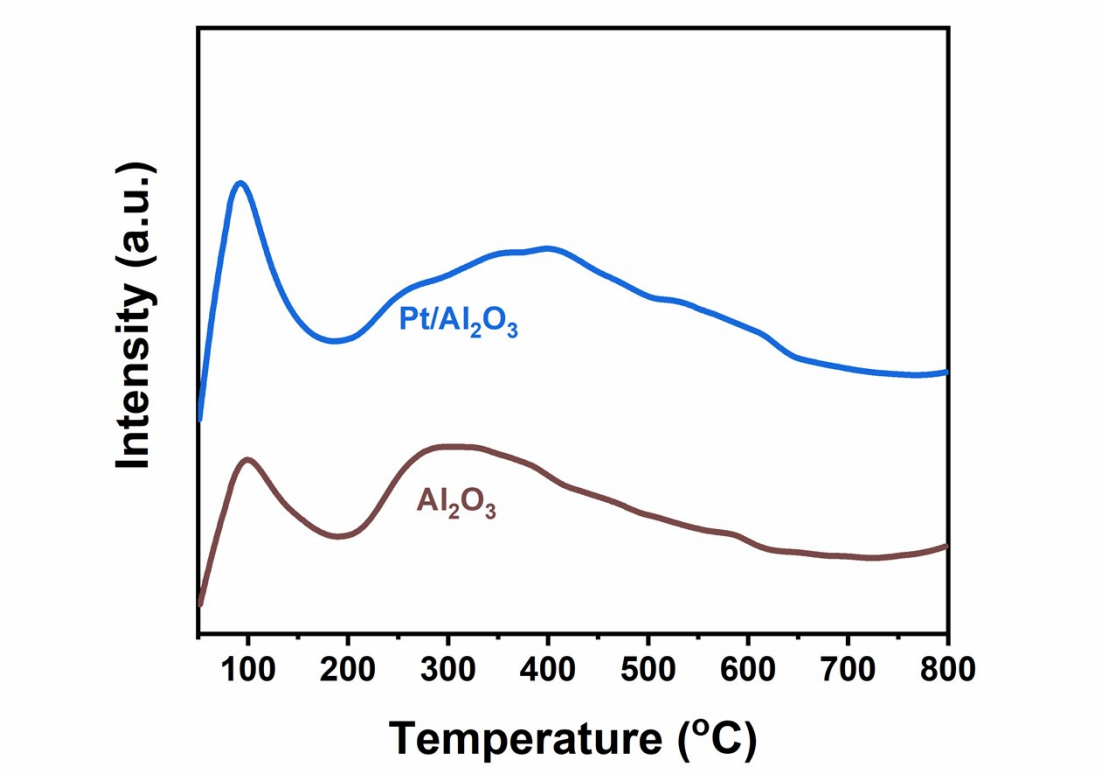


Figure S6. H_2-TPD profiles of the Pt/Al_2O_3 and Al_2O_3.

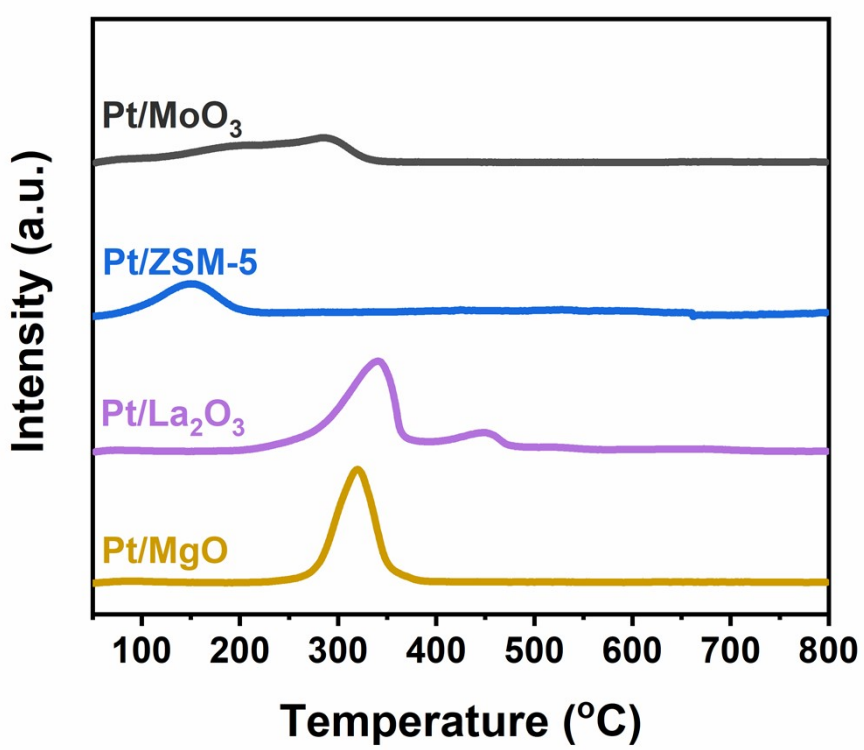


Figure S7. H_2-TPD profiles of the Pt-based catalysts.

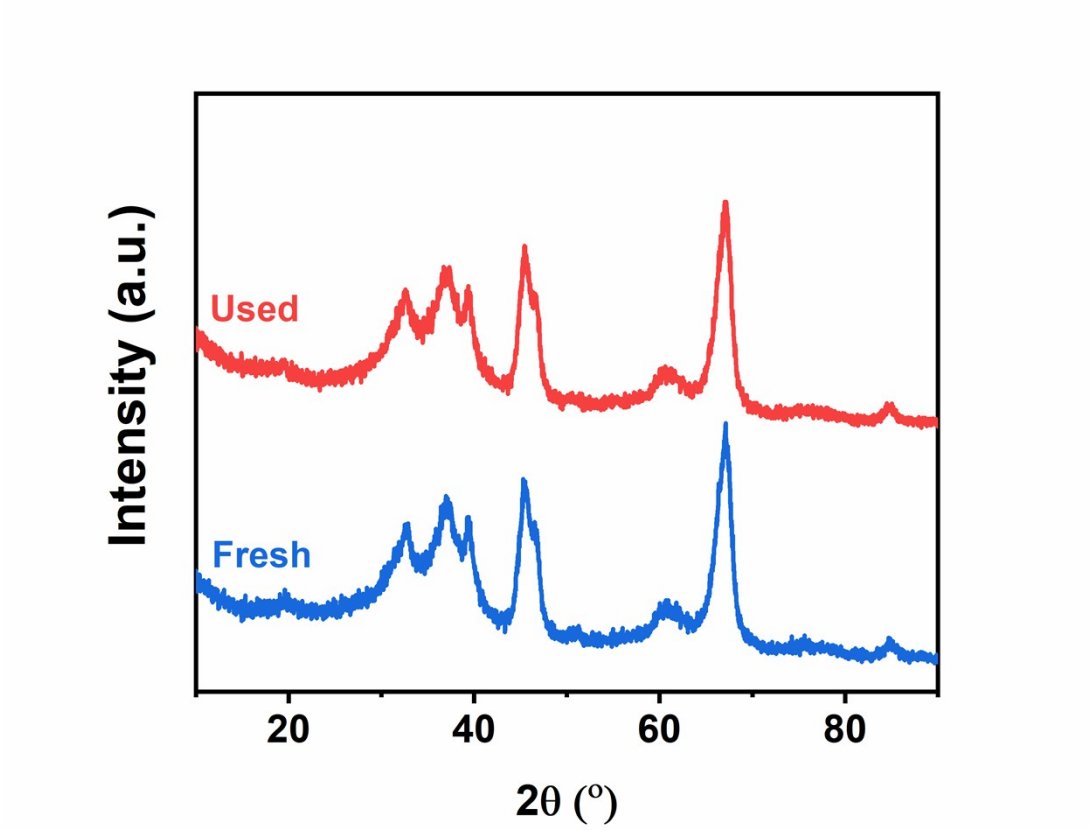


Figure S8. XRD patterns of the fresh and used Pt/$La_{0.1}$-Al_2O_3 catalysts.

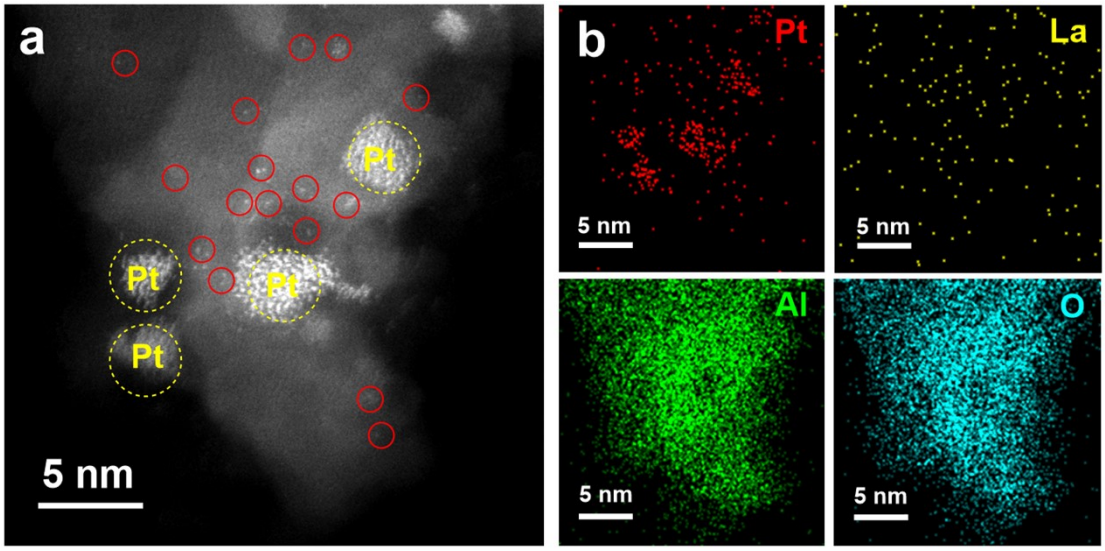


Figure S9. AC-HADDF-STEM analysis of the used Pt/$La_{0.1}$-Al_2O_3 catalyst. (a) AC-HADDF-STEM image. (b) The corresponding EDS elemental mapping.

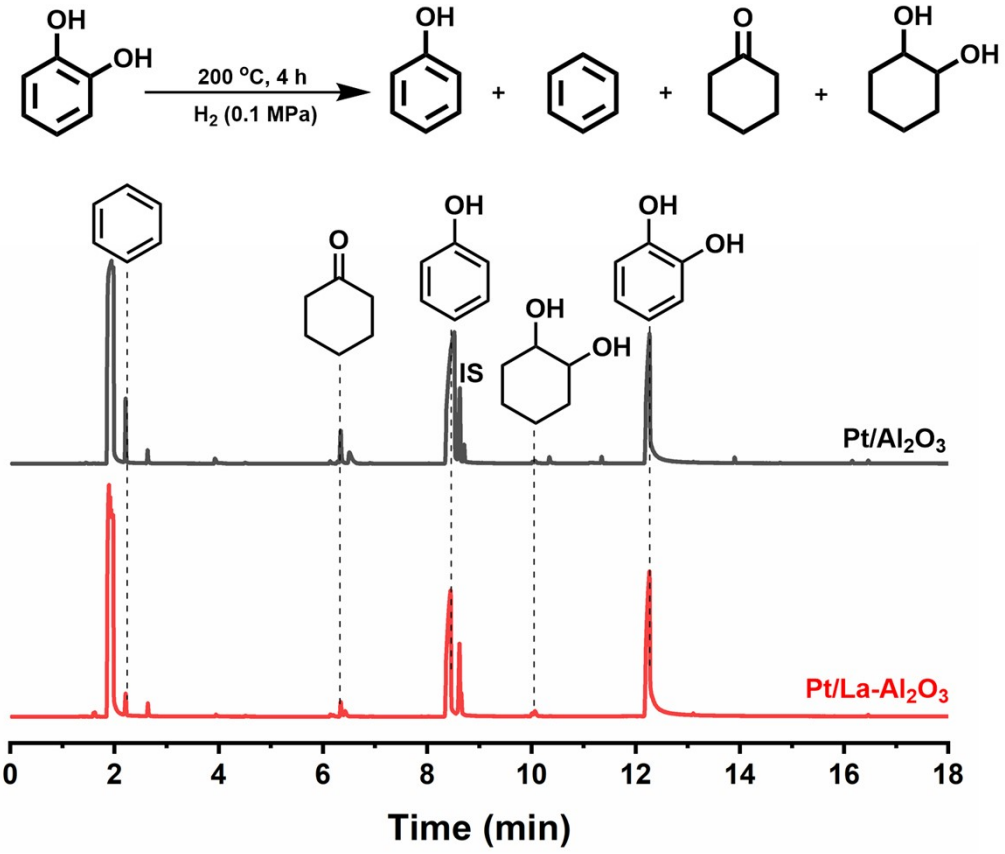


Figure S10. GC trace of the liquid mixture. Reaction conditions: Catechol (0.5 mmol), Pt catalysts (0.02 g), H_2O (2.0 mL), 200 °C, 4.0 h, 0.1 MPa H_2, 800 rpm.

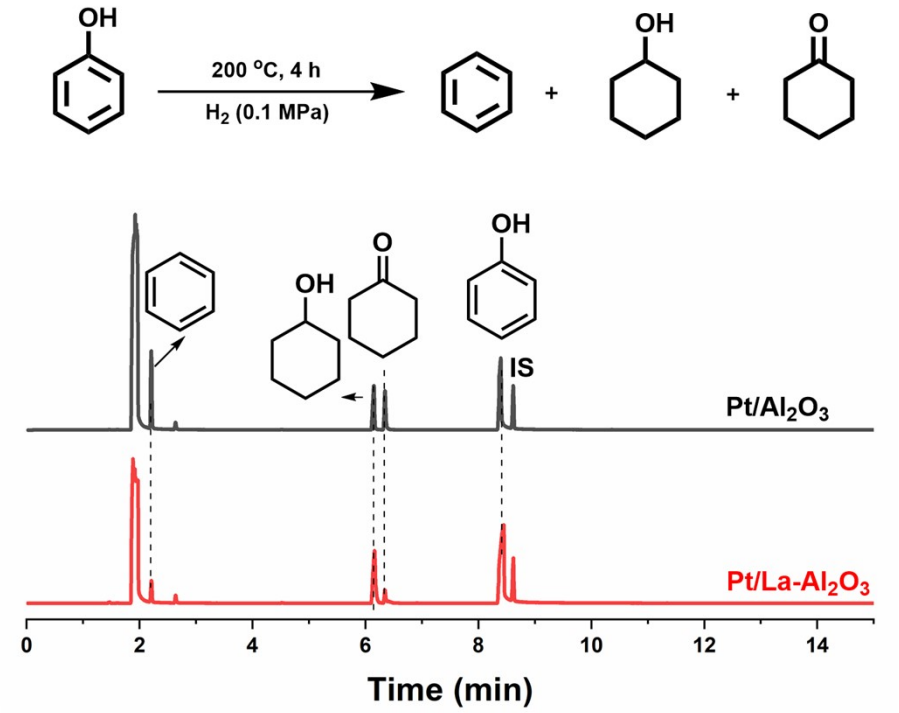


Figure S11. GC trace of the liquid mixture. Reaction conditions: Phenol (0.5 mmol), Pt catalysts (0.02 g), H_2O (2.0 mL), 200 °C, 4.0 h, 0.1 MPa H_2, 800 rpm.

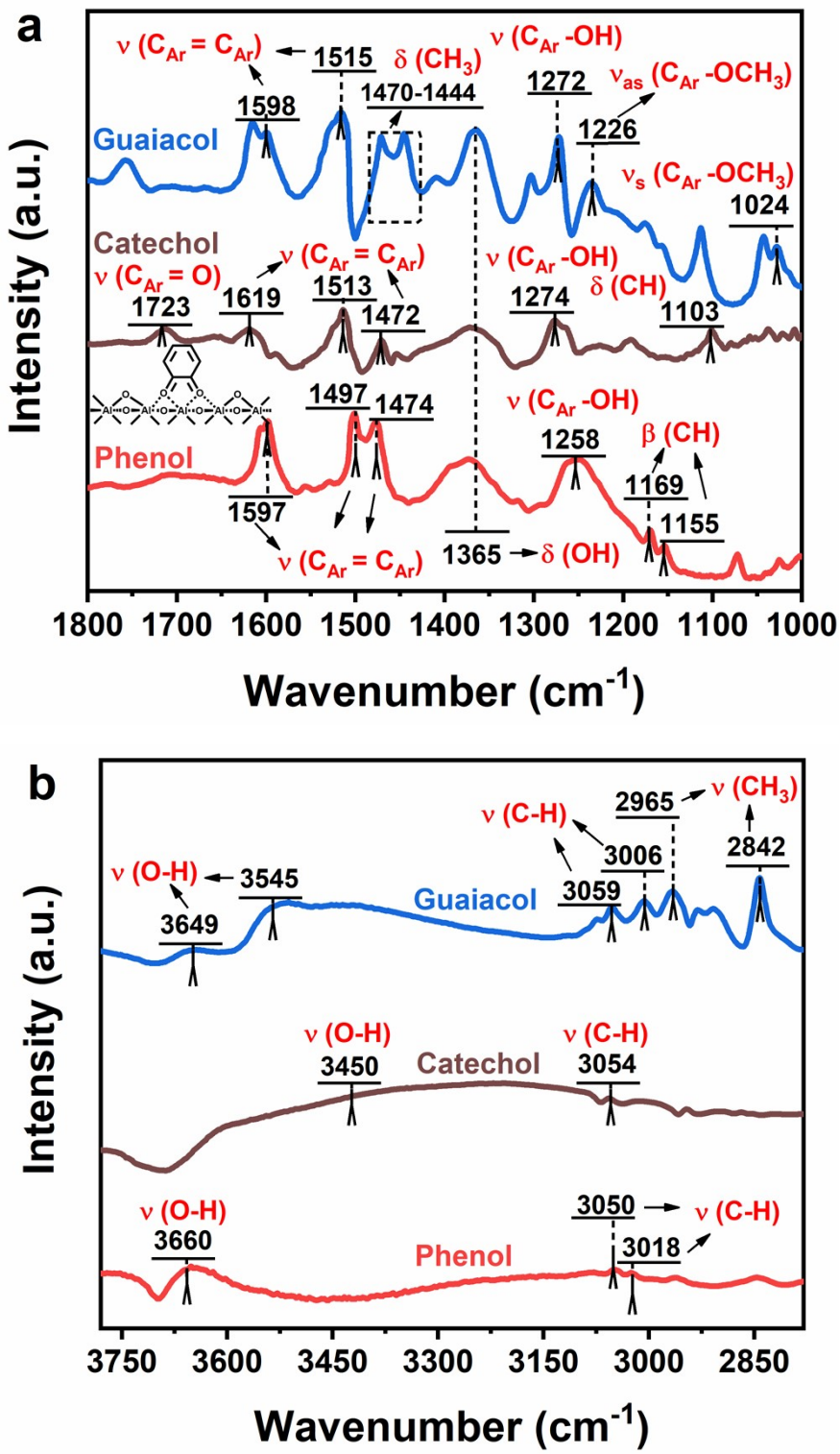


Figure S12. In situ DRIFT characterization of the Pt/$La_{0.1}$-Al_2O_3 catalyst on exposure to phenols recorded in the ranges of (a) 1800-1700 cm^{-1} and (b) 3780-2780 cm^{-1}. The image inserted in (a) shows the chemical structural formula of the benzoquinone formed by part of the catechol and metal Al. Reaction conditions: phenols (10 uL), Pt/$La_{0.1}$-Al_2O_3 (0.01 g), H_2O (10 uL), 0.1 MPa H_2, and 30 °C.

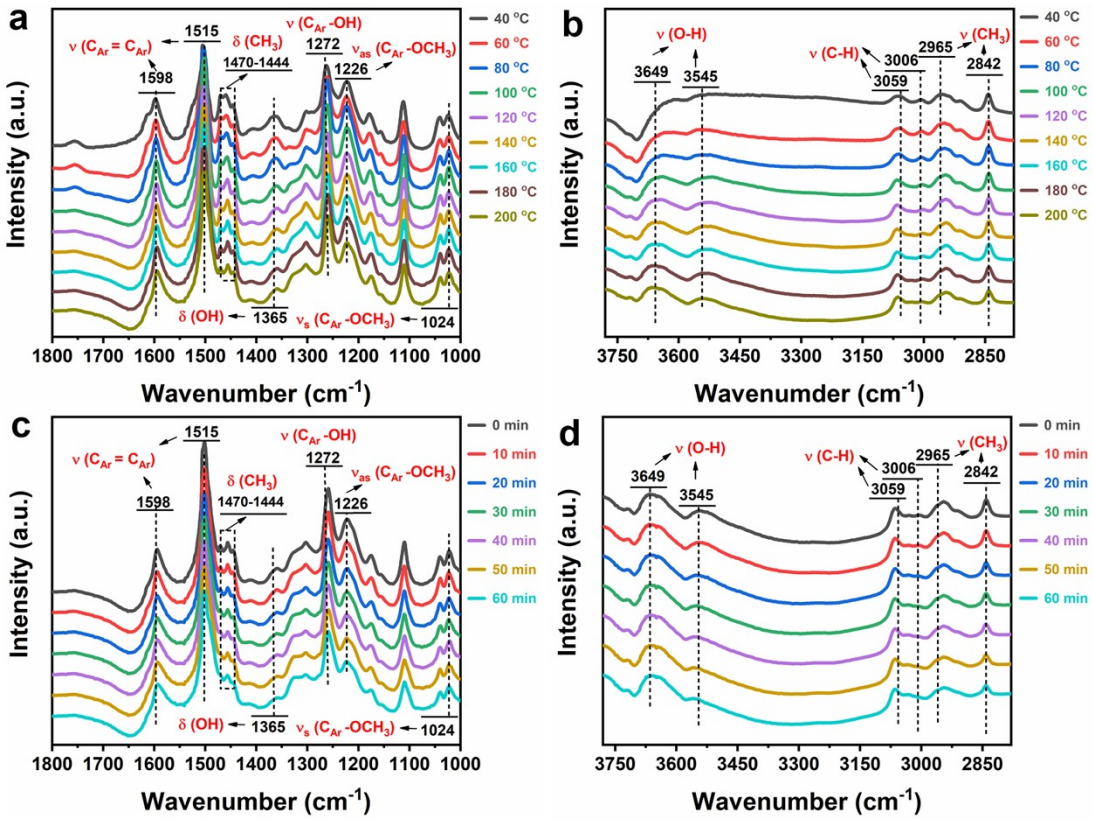


Figure S13. In situ DRIFT characterization. (a) and (b) In situ DRIFT spectra of the Al_2O_3 catalyst on exposure to guaiacol recorded in the ranges of (a) 1800-1700 cm^{-1} and (b) 3780-2780 cm^{-1} at different temperatures. Reaction conditions: guaiacol (10 uL), Al_2O_3 (0.01 g), H_2O (10 uL), 0.1 MPa H_2, and 10 min. (c) and (d): In situ time-resolved DRIFT spectra of the Al_2O_3 catalyst on exposure to guaiacol recorded in the ranges of (c) 1800-1700 cm^{-1} and (d) 3780-2780 cm^{-1}. Reaction conditions: guaiacol (10 uL), Al_2O_3 (0.01 g), H_2O (10 uL), 0.1 MPa H_2, and 200 ^oC.

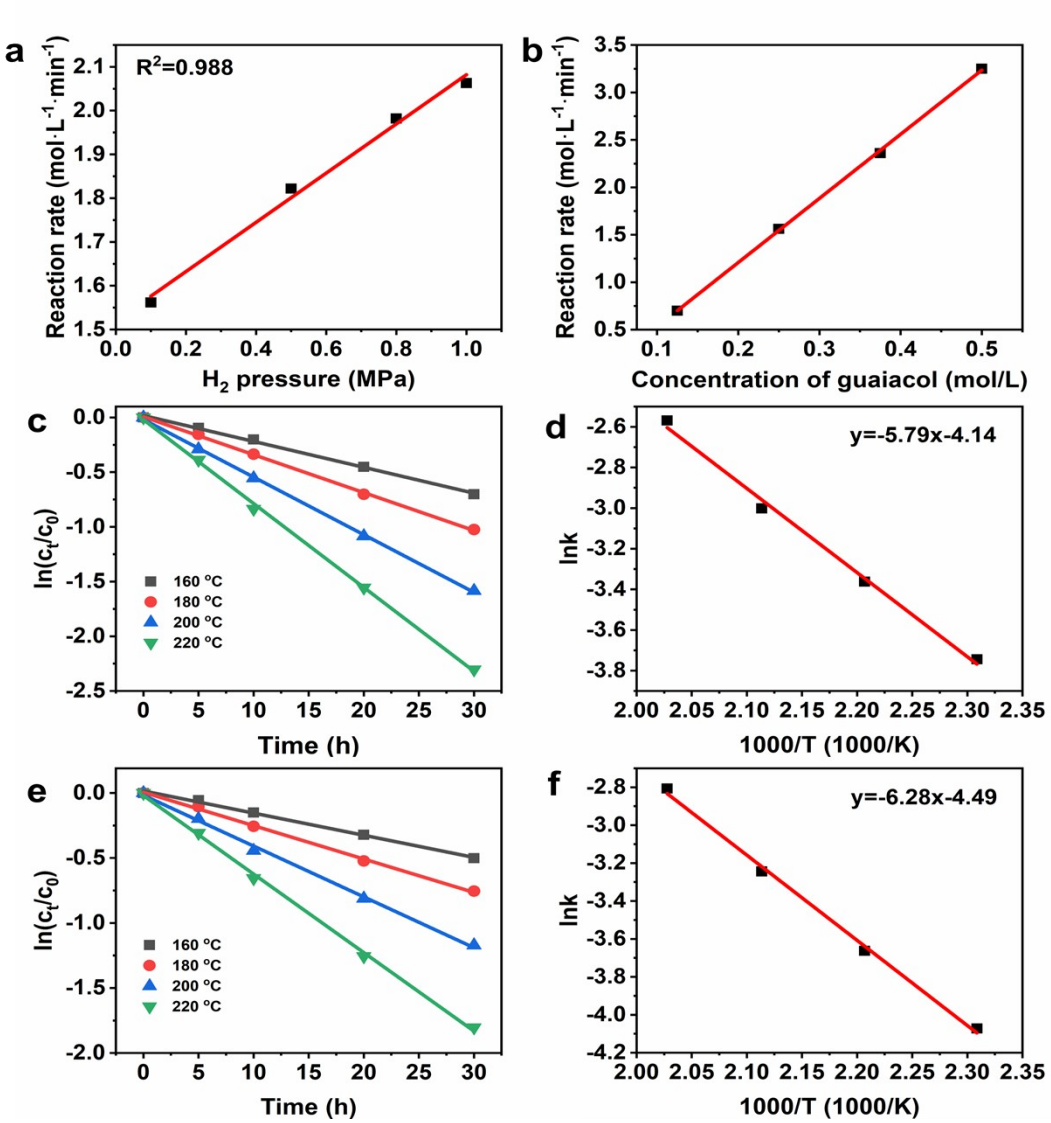


Figure S14. (a-d) Kinetic study of the HDO reactions over the Pt/$La_{0.1}$-Al_2O_3 catalyst. (a) Relationship between reaction rate of guaiacol and H_2 pressure. (b) Relationship between reaction rate of guaiacol and guaiacol concentration. (c) Relationship between $\ln(c_t/c_0)$ and reaction time at various reaction temperatures and (d) Arrhenius plot. (c-e) Kinetic study of the HDO reactions over the Pt/Al_2O_3 catalyst. (c)Relationship between $\ln(c_t/c_0)$ and reaction time at various reaction temperatures and (e) Arrhenius plot.

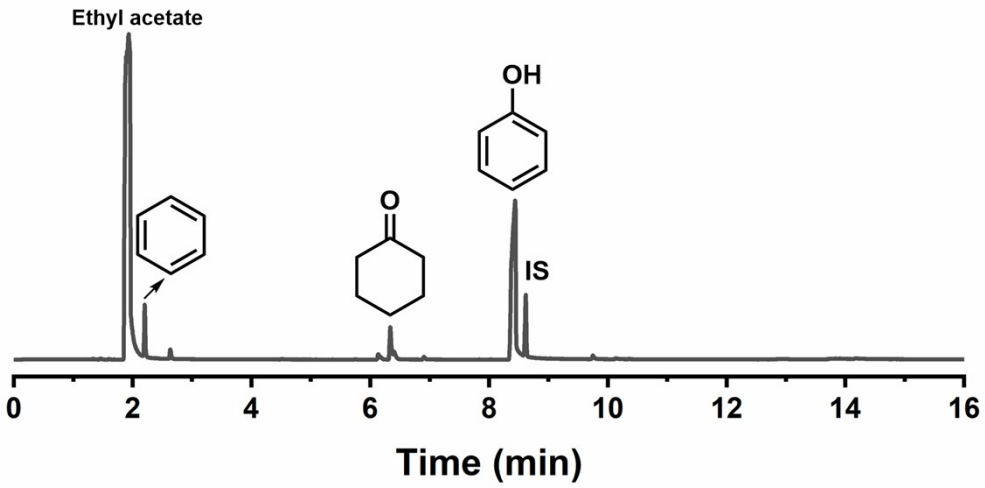


Figure S15. GC trace of the liquid mixture. Reaction conditions: 3-Methoxyphenol (0.5 mmol), Pt/$La_{0.1}$-Al_2O_3 (0.02 g), H_2O (2.0 mL), 200 °C, 4.0 h, 0.1 MPa H_2, 800 rpm.

Table S1. ICP-AES analysis for $Pt/La_x\text{-}Al_2O_3$ catalyst.

Sample	Pt (wt%)	La (wt%)
$Pt/La_{0.01}\text{-}Al_2O_3$	1.0	0.01
$Pt/La_{0.05}\text{-}Al_2O_3$	1.0	0.05
$Pt/La_{0.1}\text{-}Al_2O_3$	1.0	0.10
$Pt/La_{0.2}\text{-}Al_2O_3$	1.0	0.20
$Pt/La_{1}\text{-}Al_2O_3$	1.0	1.00
$Pt/La_{0.1}\text{-}Al_2O_3$[a]	0.99	0.10

[a]Used $Pt/La_{0.1}\text{-}Al_2O_3$ catalysts.

Table S2. XPS data of Pt/La_x-Al_2O_3 catalysts.

Sample	$Pt^{\delta+}/(Pt^{\delta+}+Pt^0)$ (%)	O_γ content (%)
Pt/Al_2O_3	0	0.168
$Pt/La_{0.01}$-Al_2O_3	28.7	0.172

Table S3. The hydrogen consumption experiments result of Pt/La_x-Al_2O_3 catalysts.

Sample	H_2 consumption (120-280 °C) (mmol/g)[b]	H_2 consumption (280-600 °C) (mmol/g)[b]	H_2 consumption $PtO_2 \rightarrow Pt$ (mmol/g)
Al_2O_3	0.018	-	0.1025
$La_{0.1}$-Al_2O_3	0.015	-	0.1025
Pt/Al_2O_3	0.010	0.168	0.1025
$Pt/La_{0.01}$-Al_2O_3	0.010	0.172	0.1025
$Pt/La_{0.1}$-Al_2O_3	0.038	0.253	0.1025
Pt/La_1-Al_2O_3	0.015	0.255	0.1025

Table S4. The hydrogen adsorption experiments result of Pt/La_x-Al_2O_3 catalysts.

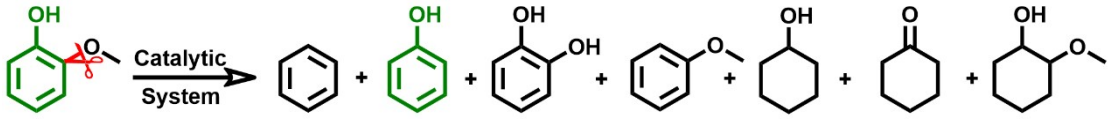
Sample	H_2 adsorption capacity (50-200 °C) (umol/g)[b]	H_2 adsorption capacity （200-800 °C） (umol/g)
Al_2O_3	3.59	9.89
Pt/Al_2O_3	6.19	14.27
$Pt/La_{0.01}$-Al_2O_3	5.93	19.62
$Pt/La_{0.1}$-Al_2O_3	4.97	32.23
Pt/La_1-Al_2O_3	4.12	18.13

Table S5. The hydrogen adsorption experiments result of Pt-based catalysts.

Sample	H_2 adsorption capacity (50-800 °C) (umol/g)[b]	Pt dispersion[a]/%
Pt/MoO_3	9.12	15.6
Pt/ZSM-5	12.02	21.1
Pt/Al_2O_3	20.46	35.8
Pt/La_2O_3	22.23	36.8
Pt/MgO	22.50	37.2
$Pt/La_{0.1}$-Al_2O_3	37.20	45.8

[a] Pt dispersion estimated from the amount of CO chemisorbed.

Table S6. Reaction of guaiacol in different solvents.



Entry[a]	Solvent	Conversion (%)	t (h)	Yield (%)							Selectivity of Phenol (%)
				Benzene	Phenol	Pyroca-techol	Ani-sole	Cyclo-hexanol	Cyclo-hexanone	2-MCH	
1	H_2O	95.8	4.0	0.4	81.6	9.7	1.5	0.0	2.0	0.3	85.1
2	methanol	0.6	4.0	0.1	0.1	0.2	0.0	0.0	0.0	0.1	16.7
3	ethanol	8.4	4.0	5.8	1.0	0.0	0.0	0.0	0.0	1.4	11.9
4	isopropanol	37.8	4.0	0.0	10.1	0.0	0.4	3.2	0.8	23.0	26.7
5	THF	2.1	4.0	0.6	0.3	0.0	0.2	0.2	0.2	0.3	14.3

[a]Reaction results are the averages of three experiments conducted in parallel. Reaction conditions: Guaiacol (0.5 mmol), $PtLa_{0.1}/Al_2O_3$ (0.02 g), solvent (2.0 mL), 200 °C, 4.0 h, 0.1 MPa H_2, 800 rpm.

References

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