Supporting Information

Fabrication of lithium phenoxide complexes for hydrogen storage evaluation

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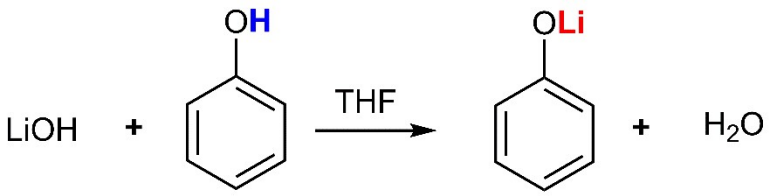
Experimental Section

Synthesis of metalorganic compound, $Li(C_6H_5O)$

$Li(C_6H_5O)$ was synthesized as illustrated in **Scheme S1** by reacting lithium hydroxide (LiOH, 98 %, Acros Organic) with phenol (C_6H_5OH, 99 %, Alfa Aesar) in a 1.1:1 molar ratio. In a typical procedure, 0.011 mol LiOH and 0.01 mol C_6H_5OH were dissolved in 30 mL of tetrahydrofuran (THF, $(CH_2)_4O$, QReC) and stirred for 24 h. After the reaction, the solvent was removed under vacuum at 100 °C, yielding a solvent-free white powder. To prepare lithium hydroxide-phenoxide and lithium phenoxide-phenol complexes, the same procedure was followed using different $LiOH/C_6H_5OH$ molar ratios of 2:1, 1:2, 1:3, 1:4, and 1:6. THF was specifically chosen over water as the reaction medium to avoid introducing excess water into the final product. Although one mole of water is generated as a byproduct during the reaction, its amount is negligible relative to the sample mass and can be easily removed, unlike when water is used as the primary solvent. Replacing water with a low surface tension solvent is preferred to avoid particle agglomeration during the drying process.[28] Additionally, THF offers a significantly lower boiling point compared to water, enabling the production of moisture-free products in a shorter time



Scheme S1. Synthetic route for the preparation of $Li(C_6H_5O)$.

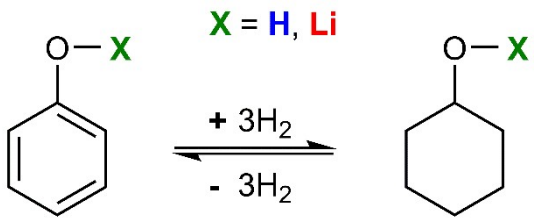
Sample characterizations

The formation of $Li(C_6H_5O)$ was confirmed by proton Nuclear Magnetic Resonance (^1H NMR) spectroscopy using a Bruker Avance 500 operating at a resonance frequency of 500 MHz with dimethyl sulfoxide-*d6* (DMSO-*d6*: 2.50 ppm) as the deuterated solvent. Chemical shifts were reported in ppm relative to an external reference of tetramethylsilane (TMS). Structural characterization of the synthesized samples was performed using X-ray powder diffraction (XRD) on a Bruker D8 Advance diffractometer operated in continuous scanning mode with a copper (Cu) X-ray source (λ= 1.5406 Å; 40 kV; 40 mA). Diffraction patterns were recorded over a 2θ range of 5°–80° at a scan rate of 2 °C min^{-1} and a step size of 0.02°. The vibrational properties of key chemical bonds, particularly O–H, C–O, and Li–O, were analyzed using Fourier Transform Infrared (FTIR) spectroscopy on a Shimadzu IRSpirit (A224160) in the spectral range of 400–4000 cm^{-1}.

Catalytic hydrogenation and dehydrogenation

In this study, solvent-free (de)hydrogenation were employed to eliminate the contribution of solvent dead weight contribution which would otherwise reduce the overall gravimetric hydrogen storage density of the system.The hydrogen storage performance of as-synthesized

samples was evaluated using a metal catalyst to sample molar ratio of 1:10. The solid mixture was prepared by thoroughly grinding the synthesized sample with the selected commercial catalyst before transferring it into a stainless-steel tube reactor. Hydrogenation was performed isothermally at 90 °C under 30 bar of H_2 using a custom-designed volumetric release system for several hours. Whilst the hydrogenation was carried out using the as-synthesized samples (1.1:1, 2:1, 1:2, and 1:6), direct dehydrogenation reaction was performed on the hydrogenated products at 140 °C under vacuum to promote the hydrogen release. The products of hydrogen uptake and release were analyzed and quantified by ^{1}H NMR spectroscopy. For comparative evaluation, the performance of newly synthesized samples was assessed alongside that of pristine phenol (C_6H_5OH, 99 % Alfa Aesar) and cyclohexanol ($C_6H_{11}OH$, 98 %, QReC), using various commercial noble metal catalysts, namely, 5 wt % Ru/Al_2O_3 (99 %, Sigma Aldrich), 5 wt % Ru/Al_2O_3 (99 %, Acros Organic), 5 wt % Pd/C (99 %, Alfa Aesar), and 5 wt % Pt/C (99 %, Sigma Aldrich). Both the unsaturated aromatic ring in C_6H_5OH and its lithiated form, $Li(C_6H_5O)$, are capable of absorbing up to six equivalents of hydrogen atoms during hydrogenation, as illustrated in **Scheme S2**.



Scheme S2. Hydrogenation and dehydrogenation of $Li(C_6H_5O)$.

The reaction conversion and product selectivity were determined using ^{1}H NMR spectroscopy. For each compound, the integral of a selected proton signal was used to calculate conversion and selectivity.

The conversion of the substrate was calculated as:

$$\text{Percentage of remaining substrate, } S\ (\%) = (I_0/\Sigma I_a) \times 100\%$$

$$\text{Conversion } (\%) = 100 - S$$

where I_0 is the integral of the substrate and I_a is the sum of the integrals of all products including the remaining substrate

The selectivity of each product was calculated as:

$$\text{Selectivity } (\%) = (I_i/\Sigma I_k) \times 100\%$$

Where I_i is the integral of the individual product and I_k is the sum of the integrals of all products.

Spectroscopic data:

NMR multiplicities are reported as singlet (s), doublet (d), triplet (t), and multiplet (m). FTIR band are assigned as stretching (ν), and bending (δ) with peak intensities reported as weak (w), medium (m), strong (s), and broad (b).

Lithium phenoxide (1.1:1) LiOH/C_6H_5OH: **^{1}H NMR** (500 MHz, DMSO-d_6) δ = 6.91 – 6.85 (t, *J*=7.6, 2H, CH), 6.50 – 6.44 (d, *J*=7.9, 2H, CH), 6.23 – 6.16 (t, *J*=7.2, 1H, CH). **FTIR** (KBr cm^{-1}): 3057, 3022 νC–H (w), 1266 νC–O (s), 598 νLi–O (s), 434 δLi–O (m)

Lithium-rich complex (2:1) LiOH/C_6H_5OH: **^{1}H NMR** (500 MHz, DMSO-d_6) δ = 6.88 – 6.76 (t, *J*=7.5, 2H, CH), 6.44 – 6.30 (d, *J*=7.9, 2H, CH), 6.15 – 6.06 (t, *J*=7.3, 1H, CH). **FTIR** (KBr cm^{-1}): 3057, 3022 νC–H (w); 1266 νC–O (s); 598 νLi–O (s); 433 δLi–O (s)

Phenol-rich complex (1:2) LiOH/C_6H_5OH: **^{1}H NMR** (500 MHz, DMSO-d_6) δ = 6.98 – 6.88 (t, *J*=7.6, 2H, CH), 6.59 – 6.50 (d, *J*=7.8, 2H, CH), 6.31 – 6.24 (t, *J*=7.2, 1H, CH). **FTIR** (KBr cm^{-1}): 3309 νO–H; (w,b); 3057, 3022 νC–H (w); 1266 νC–O (s); 598 νLi–O (m); 434 δLi–O (w)

Phenol-rich complex (1:3) LiOH/C_6H_5OH: **^{1}H NMR** (500 MHz, DMSO-d_6) δ = 7.85 (s, 1H, OH), δ = 7.05 – 6.98 (t, *J*=7.6, 2H, CH), 6.71 – 6.64 (d, *J*=7.9, 2H, CH), 6.52 – 6.45 (t, *J*=7.2, 1H, CH). **FTIR** (KBr cm^{-1}): 3309 νO–H; (b); 1370 δO–H (m); 3057, 3022 νC–H (w); 1242 νC–O (s,b); 598 νLi–O (m); 430 δLi–O (w)

Phenol-rich complex (1:4) LiOH/C_6H_5OH: **^{1}H NMR** (500 MHz, DMSO-d_6) δ = 8.82 (s, 1H, OH), 7.10 – 6.96 (t, *J*=7.7, 2H, CH), 6.72 – 6.62 (d, *J*=8.0, 2H, CH), 6.56 – 6.49 (t, *J*=7.2, 1H, CH). **FTIR** (KBr cm^{-1}): 3309 νO–H; (b); 1370 δO–H (m); 3057, 3022 νC–H (w); 1235 νC–O (s,b); 435 δLi–O (w)

Phenol-rich complex (1:6) LiOH/C_6H_5OH: **^{1}H NMR** (500 MHz, DMSO-d_6) δ = 9.67 (s, 1H, OH), 7.13 – 7.05 (m, 2H, CH), 6.79 – 6.72 (m, 2H, CH), 6.67 – 6.61 (m, 1H, CH). **FTIR** (KBr cm^{-1}): 3296 νO–H; (b); 1370 δO–H (m); 3057, 3022 νC–H (w); 1235 νC–O (s); 435 δLi–O (w)

Phenol C_6H_5OH: **^{1}H NMR** (500 MHz, DMSO-d_6) δ = 9.39 (s, 1H, OH), 7.21 – 7.13 (m, 2H, CH), 6.83 – 6.77 (m, 2H, CH), 6.77 (m, 1H, CH). **FTIR** (KBr cm^{-1}): 3345 νO–H, (b); 1370 δO–H (m); 3047, 3021 νC–H (w); 1232 νC–O (s).

Cyclohexanol $C_6H_{11}OH$: **^{1}H NMR** (500 MHz, DMSO-d_6) δ = 4.66 (s, 1H, OH), 3.45 – 3.30 (m, 1H, CH), 1.81 – 1.57 (m, 4H, CH_2), 1.49 – 1.40 (m, 1H, CH_2), 1.24 – 1.01 (m, 5H, CH_2).

Table S1. Solid-state hydrogen absorption of $Li(C_6H_5O)$ and different molar ratios of $LiOH/C_6H_5OH$ under 30 bar H_2, aided by a 1:10 catalyst to sample ratio. Solvent-less hydrogen absorption of C_6H_5OH was carried out under the same conditions for comparison purposes.

Entry	Sample ($LiOH/C_6H_5OH$)	Hydrogen absorption		
		Catalyst (5 wt%)	T_h (°C)/ time (h)	Conversion[b] (%)
1	C_6H_5OH	Ru/Al_2O_3	90/ 3.5	95.6[c]
2	1.1:1 or $Li(C_6H_5O)$[a]	Ru/Al_2O_3	90/ 3.5	97.0
3			60/ 3.5	99.6
4		Rh/Al_2O_3	90/ 3.5	95.1
5		Pd/C	90/ 3.5	93.0
6		Pt/C	90/ 3.5	81.2
7	2:1[a]	Ru/Al_2O_3	90/ 3.5	99.1
8			60/ 3.5	99.7
9	1:2[a]	Ru/Al_2O_3	90/ 3.5	96.3
10	1:6[a]	Ru/Al_2O_3	90/ 3.5	87.0

[a] Hydrogenation reaction was performed using the as-synthesized samples. [b] the reaction conversion was quantified by using ^1H NMR. [c] data obtained in our previous work.[1]

Table S2. Solid-state hydrogen desorption of $C_6H_{11}OH$, hydrogenated sample of $Li(C_6H_5O)$, and different molar ratios of $LiOH/C_6H_5OH$ under vacuum.

Entry	Sample ($LiOH/C_6H_5OH$)	Hydrogen desorption		
		Catalyst (5 wt%)	T_d (°C)/ time (h)	Conversion[b] (%)
1	$C_6H_{11}OH$	Ru/Al_2O_3	140/ 10	15.2[c]
2		Rh/Al_2O_3	140/ 10	14.9[c]
3			260/ 10	21.7
4		Pd/C	140/ 10	20.8
5			260/ 10	97.5[d]
6		Pt/C	140/ 10	33.6
7			260/ 10	92.1[d]
8	1.1:1 or $Li(C_6H_5O)$[a]	Ru/Al_2O_3	140/ 10	34.4
9		Rh/Al_2O_3	140/ 10	31.9
10		Pd/C	140/ 10	35.9
11		Pt/C	140/ 10	29.8
12	2:1[a]	Ru/Al_2O_3	140/ 10	48.1
13	1:2[a]	Ru/Al_2O_3	140/ 10	29.5
14	1:6[a]	Ru/Al_2O_3	140/ 10	20.0

[a] Direct dehydrogenation reaction was performed using the hydrogenated products. [b] the reaction conversion was quantified by using ^1H NMR. [c] data obtained in our previous work.[1] [d] exhibited high selectivity toward benzene formation.

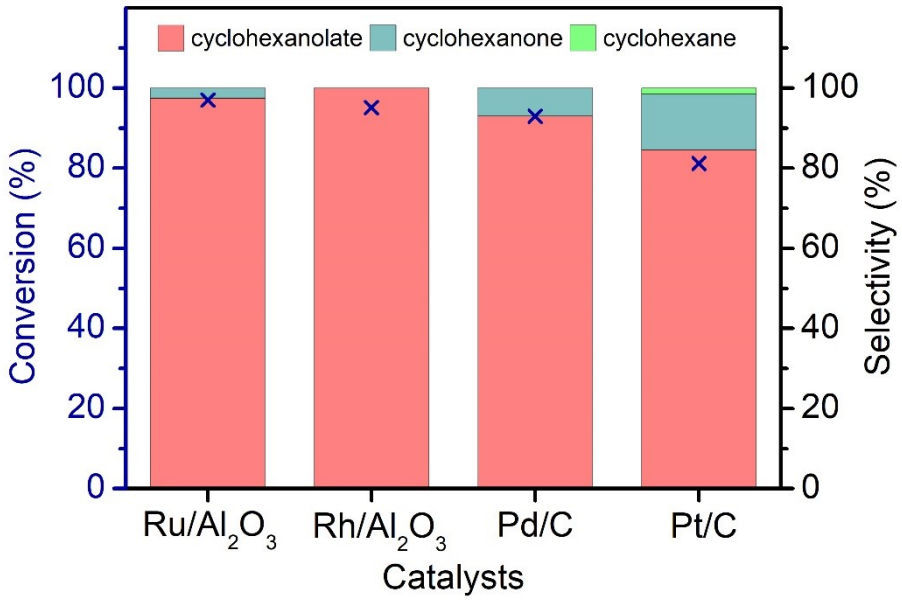


Figure S1. Product selectivity from hydrogenation of as-synthesized 1.1:1 $LiOH/C_6H_5OH$ at 90 °C, 3.5 h catalyzed by 5 wt% metal catalysts with a molar ratio of metal catalyst to phenoxide of 1:10.

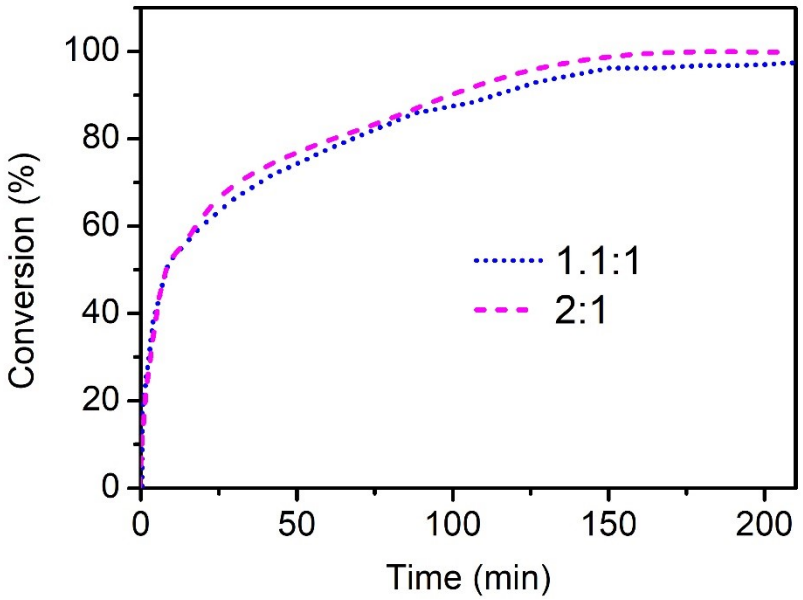


Figure S2. Hydrogen uptake curves of as-synthesized 1.1:1 and 2:1 $LiOH/C_6H_5OH$ over 5 wt% Ru/Al_2O_3 under 30 bar of H_2 at 90 °C with a molar ratio of metal catalyst to phenoxide of 1:10.

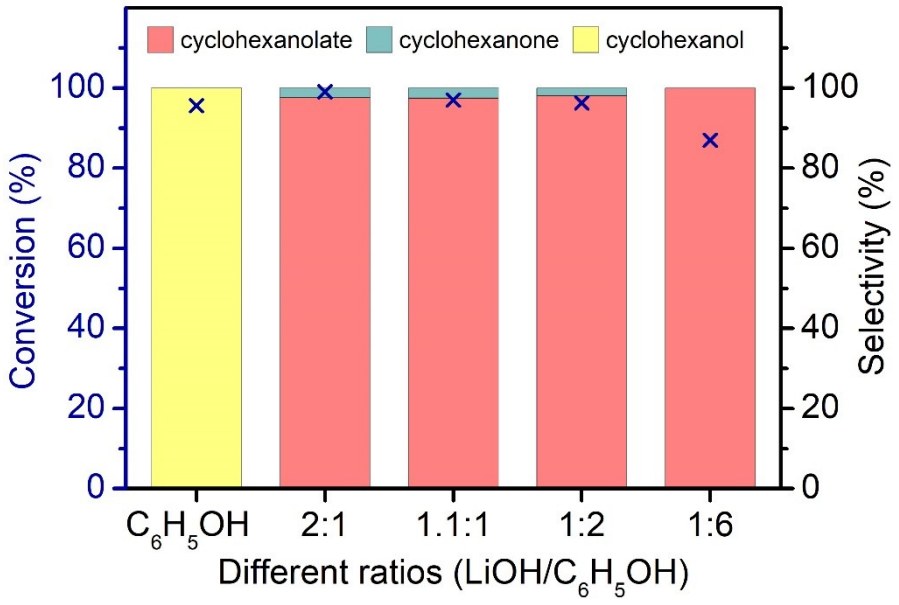


Figure S3. Product selectivity from hydrogenation of as-synthesized different ratios of $LiOH/C_6H_5OH$ at 90 °C, 3.5 h catalyzed by 5 wt% Ru/Al_2O_3 with a molar ratio of metal catalyst to phenol or phenoxide of 1:10.

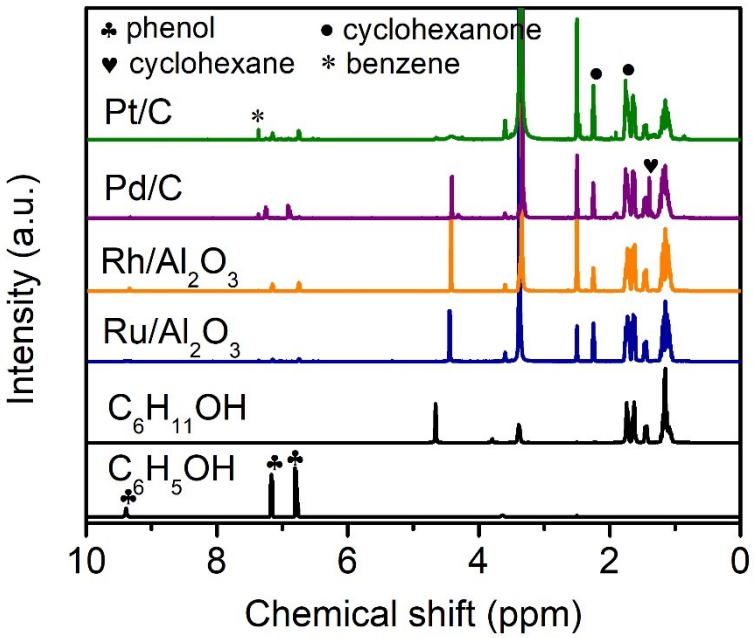


Figure S4. ^{1}H NMR spectra of the dehydrogenation of cyclohexanol at 140 °C, 10 h over different metal catalysts with a molar ratio of metal catalyst to cyclohexanol of 1:10 in DMSO-*d6*.

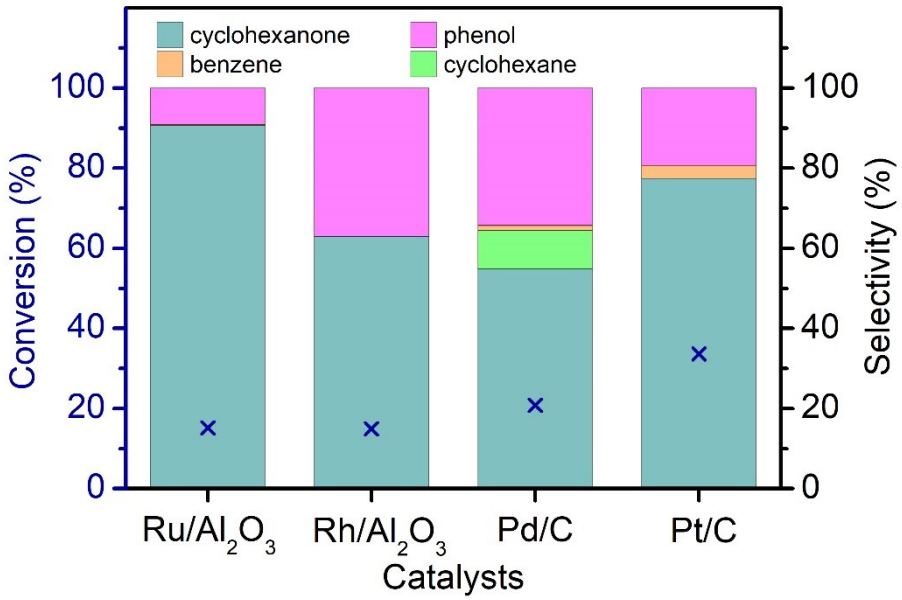


Figure S5. Product selectivity from the dehydrogenation of cyclohexanol at 140 °C, 10 h over different metal catalysts with a molar ratio of metal catalyst to cyclohexanol of 1:10.

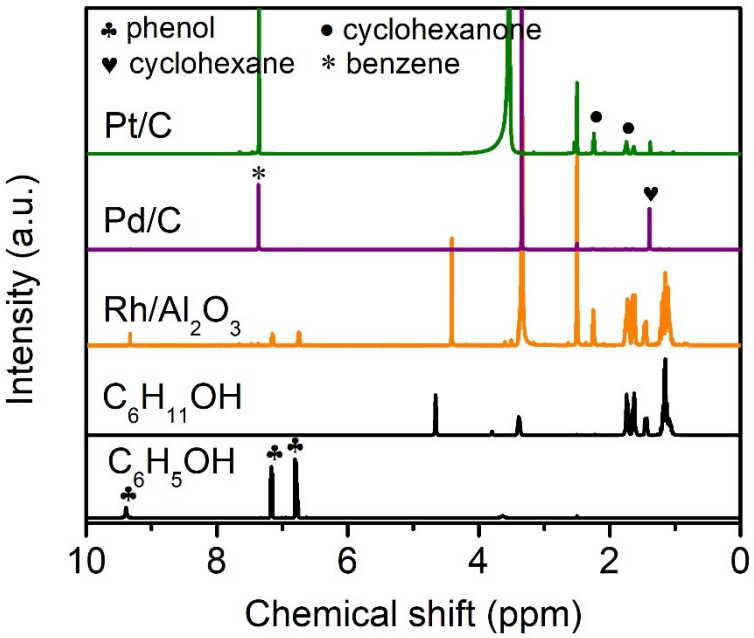


Figure S6. ^{1}H NMR spectra of the dehydrogenation of cyclohexanol at 260 °C, 10 h over different metal catalysts with a molar ratio of metal catalyst to cyclohexanol of 1:10 in DMSO-*d6*.

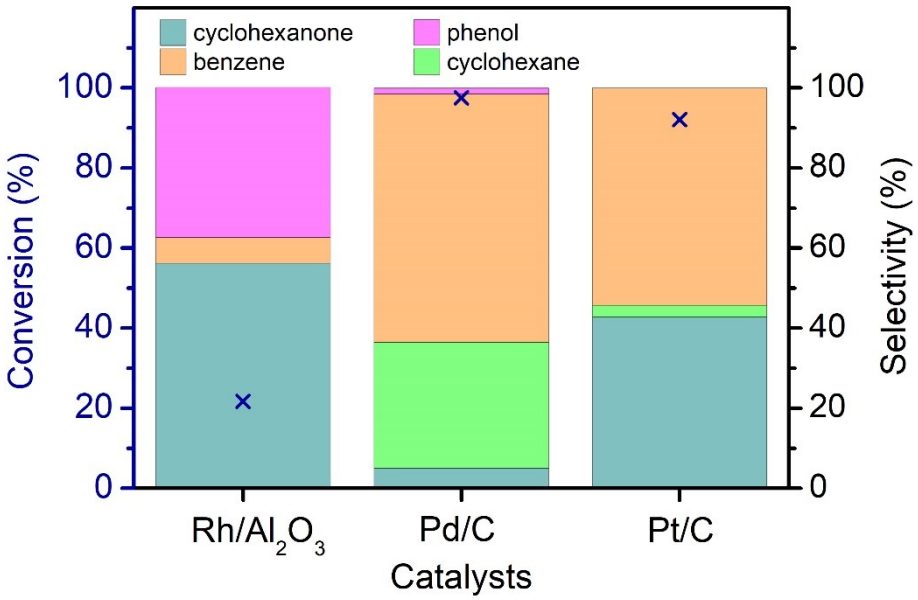


Figure S7. Product selectivity from the dehydrogenation of cyclohexanol at 260 °C, 10 h over different metal catalysts with a molar ratio of metal catalyst to cyclohexanol of 1:10.

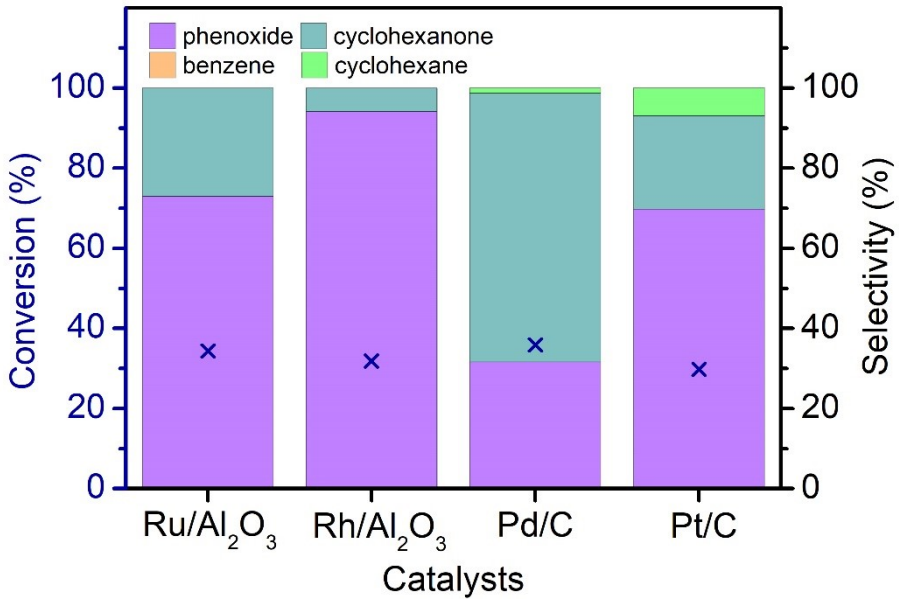


Figure S8. Product selectivity from the dehydrogenation of hydrogenated $Li(C_6H_5O)$ at 140 °C, 10 h catalyzed by 5 wt% metal catalysts.

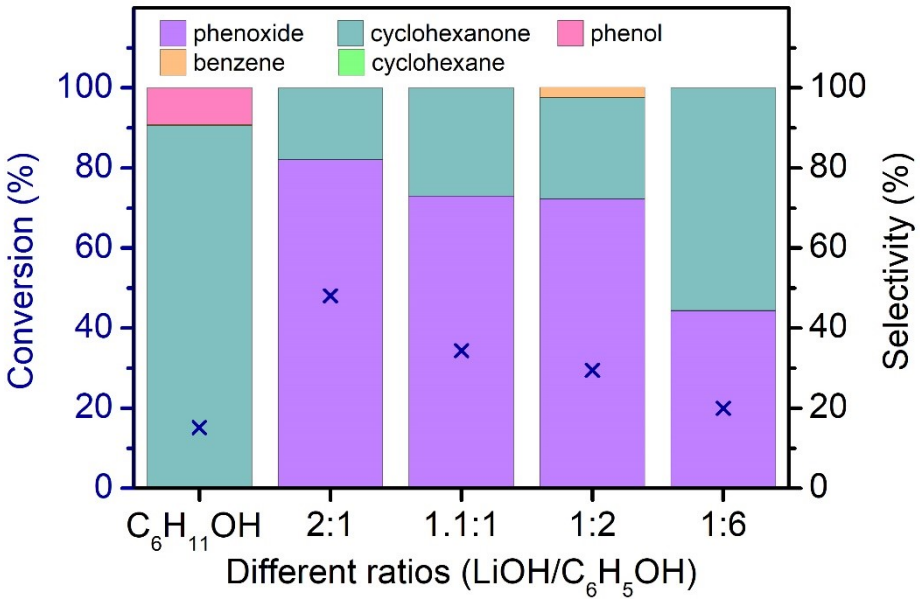


Figure S9. Product selectivity from the dehydrogenation of hydrogenated samples synthesized from different ratios of $LiOH/C_6H_5OH$ at 140 °C, 10 h catalyzed by 5 wt% metal catalysts.

Reference

1. N. I. Nordin, K. C. Tan, H. Wen, X. Ju, W. Zhou, H. Wu, T. He, P. Chen and Y. S. Chua, *ACS Appl. Energy Mater.*, 2025, 8, 6270–6279.