Supporting Information

Selective hydrogenation of guaiacol to 2-methoxycyclohexanone over supported Pd catalysts

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Table S1. Previous studies on selective hydrogenation of phenol (published after 2020) and methoxyphenols (published after 2010).

Entry	Substrate	Year of publication	Catalyst	$n_{metal}/n_{substrate}$ [mol%]	Temp. [°C]	Time [h]	H_2 pressure [MPa]	Solvent	Conv. [%]	Yield [%]	Ref.
1	Phenol	2024	Pd/ACET	0.2	343	3	0.1	Water	97.3	97.2	S1
2		2023	Pd^{2+}@CN	1.2	373	0.5	0.1	Cyclohexane	99	93	S2
3		2023	$Pd_{4.85}Ru_{0.15}$/ZrHP	0.3	373	1	0.1	Cyclohexane	97.9	97.0	S3
4		2023	Pd@mCeO_2	1.9	353	0.83	1	Dichloromethane	96.3	91.8	S4
5		2023	Pd-$Co_{0.3}$/mSiO_2	9.1	353	1	1	Dichloromethane	100	95	S5
6		2022	Ni@C-400	0.03	393	2	2	Water	100	100	S6
7		2022	Pd@CNFs-0.3	1.77	358	1	0.1	Cyclohexane	97.8	90.7	S7
8		2022	Rh-CoO_x/SiO_2	0.4	333	1.7	1	EtOH	98.1	97.5	S8
9		2022	Pt@Al_3-mSiO_2	1.2	383	1.5	1	Dichloromethane	100	96	S9
10		2021	Pd@HMSNs	3.2	323	4	0.1	Water	99	97	S10
11		2021	Pd@mpg-C_3N_4	5.0	373	1	0.1	Water	99	98	S11
12		2021	Pd@CN-H	0.8	353	0.83	0.1	Cyclohexane	99.8	90.7	S12
13		2021	Pd/NH_2-SBA-15	2.0	353	2	0.1	Water	98.0	97.6	S13
14		2021	Pd/pol-NH_2	5.0	373	2	0.3	Water	99.5	99.0	S14
15		2020	Pd/Al_2O_3-La_2O_3-CeO_2	0.9	353	6	0.3	Cyclohexane	99.8	96.1	S15
16		2020	Pd@CN-rGO-15	2.1	353	1.3	0.1	Water	97.2	94.0	S16
17		2020	NiCo/Mg_xNi_yO	7.0	453	2.5	2	Hexane	99.9	99.8	S17
18		2020	Rh@HMSNs	0.03	318	3	0.5	EtOH	90.6	87.5	S18
19			Pd/TiO_2	0.6	373	1	1 (r.t.)	Water	99.4	91.4	This work

Entry	Substrate	Year of publication	Catalyst	$n_{metal}/n_{substrate}$ [mol%]	Temp. [°C]	Time [h]	H_2 pressure [MPa]	Solvent	Conv. [%]	Yield [%]	Ref.
20	4-Methoxy-phenol	2022	$Rh-CoO_x/SiO_2$	1.2	100	24	1	EtOH	76.9	72.7	S8
21		2018	Rh/SiO_2	0.5	25	28	0.2	Cyclohexane	99	75	S19
22		2018	RuO_2-MCM-41	0.3	100	24	1	Water	100	20	S20
23		2016	Rh@SiCN	2.0	25	11	0.6	Water	95	38	S21
24		2015	Pd/HAP	2.0	75	3.5	0.1	Water	100	100	S22
25		2013	Pd/IL-like copolymer + $H_3PW_{12}O_{40}$	10	100	18	0.2	Water	100	45	S23
26			Pd/TiO_2	0.6	100	16	1 (r.t.)	Water	90.9	85.2	this work
27	Guaiacol	2024	Rh/C	0.3	40	3	1	Water	-	26.1	S24
28		2018	Ru-MCM-41	0.3	100	24	1	Water	95	19	S20
29		2018	MPF-PPI-G3-Pd	2.3	200	3	5	Water	75	21	S25
30		2017	m-Pd/C	2.1	130	15	2	Dichloromethane + water	100	10.2	S26
31		2016	$Pd/\gamma-Al_2O_3$	6.9	60	12	2	Water	56.9	33.2	S27
32		2016	Rh@SiCN	2.0	25	15	0.6	Water	90	36	S21
33		2015	Pd/HAP	2.0	75	24	0.1	Water	37.2	37	S22
34			Pd/TiO_2	0.6	100	1.5	1 (r.t.)	Water	93.8	64.3	This work
35	2,6-Dimethoxy-phenol	2015	Pd/HAP	2.0	75	24	0.1	Water	0.5	0	S22
36			Pd/TiO_2	0.6	100	24	1 (r.t.)	Water	28.8	7.2	This work

Abbreviations: ACET = acetylene black; HMSN = hollow mesoporous silica nanoreactors; rGO = reduced graphene oxide, HAP = hydroxyapatite, MPF-PPI-G3 = mesoporous phenol formaldehyde polymer modified with a third generation poly(propylene imine) dendrimer.

Table S2. List of reagents used in this study.

reagent	Supplier	Purity [%]
$PdCl_2$	FUJIFILM Wako Pure Chemical Co.	> 99.0
$Pd(OCOCH_3)_2$	FUJIFILM Wako Pure Chemical Co.	> 97.0
$Pd(NO_3)_2$	FUJIFILM Wako Pure Chemical Co.	99.9
$Pd(acac)_2$	FUJIFILM Wako Pure Chemical Co.	> 98.0
$Pd(NH_3)_4Cl_2$	Sigma-Aldrich Co.	> 98.0
Acetone	FUJIFILM Wako Pure Chemical Co.	> 99.5
Guaiacol	Tokyo Chemical Industry Co., Ltd.	> 98.0
1,4-Dioxane	FUJIFILM Wako Pure Chemical Co.	> 99.5
2-Methoxyethanol	FUJIFILM Wako Pure Chemical Co.	> 99.0
2-Methoxycyclohexanone	Tokyo Chemical Industry Co., Ltd.	> 95.0
(1*S*,2*S*)-(+)-Methoxycyclohexanol	Alfa Aesar Co.	> 97.0
Cyclohexanone	FUJIFILM Wako Pure Chemical Co.	> 99.0
Cyclohexanol	FUJIFILM Wako Pure Chemical Co.	> 98.0
Phenol	FUJIFILM Wako Pure Chemical Co.	> 99.0
Methanol	Kanto Chemical Co., Inc.	> 99.8
Methoxycyclohexane	Tokyo Chemical Industry Co., Ltd.	> 98.0
Anisole	Tokyo Chemical Industry Co., Ltd.	> 99.0
2-Hydroxycyclohexanone	Sigma-Aldrich Co.	> 97.0
Hydrochloric acid	FUJIFILM Wako Pure Chemical Co.	35.0-37.0
Sulfuric acid	FUJIFILM Wako Pure Chemical Co.	> 95.0
Ethanol	Kanto Chemical Co., Inc.	> 99.5
2-Propanol	FUJIFILM Wako Pure Chemical Co.	> 99.7
Tetrahydrofuran	FUJIFILM Wako Pure Chemical Co.	> 99.5
Cyclohexane	FUJIFILM Wako Pure Chemical Co.	> 98.0
Dodecane	Tokyo Chemical Industry Co., Ltd.	> 99.0
Toluene	FUJIFILM Wako Pure Chemical Co.	> 99.5
Toluene-d_8	FUJIFILM Wako Pure Chemical Co.	99.5
4-Methoxyphenol	Tokyo Chemical Industry Co., Ltd.	> 99.0
2-Ethoxyphenol	Tokyo Chemical Industry Co., Ltd.	> 99.0
Catechol	FUJIFILM Wako Pure Chemical Co.	> 99.0
o-Cresol	Tokyo Chemical Industry Co., Ltd.	> 99.0
2-(Trifluoromethyl)phenol	Tokyo Chemical Industry Co., Ltd.	> 98.0
2,6-Dimethoxyphenol	FUJIFILM Wako Pure Chemical Co.	> 98.0

Table S3. List of supports tested in this study.

Support	Supplier	BET surface area [$m^2\ g^{-1}$]	Detail information
α-Al_2O_3	FUJIFILM Wako Pure Chemical Co.	7.9	-
BN	FUJIFILM Wako Pure Chemical Co.	7.5	-
H-ZSM-5	Tosoh Co.	100	HSZ-822HOA (Si/Al=12)
CeO_2	Daiichi Kigenso Kagaku Kogyo Co., Ltd.	78	HS, calcined at 873 K for 3 h.
SiO_2	FUJI SILYSIA Chemical Ltd.	402	G6, calcined at 773 K for 1 h.
Nb_2O_5	FUJIFILM Wako Pure Chemical Co.	5.0	-
TiO_2 (anatase)	Sakai Chemical Industry Co., Ltd.	206	SSP-N-Anatase
TiO_2 (rutile)	FUJIFILM Wako Pure Chemical Co.	5.8	-
TiO_2 (P25)	Aeroxide Co.	50	P25
Activated carbon	Osaka Gas Chemicals Co., Ltd.	779	Shirasagi FAC-10
Carbon black	Cabot Co.	1280	Black Pearls 2000
Hydroxyapatite	FUJIFILM Wako Pure Chemical Co.	7.5	Monoclinic

Table S4. Hydrogenation of guaiacol over Pd catalysts with various supports.[a]

Support	Dispersion[b] [%]	Conv. [%]	Yield (C-based) [%]										C. B. [%]
			2-MCO	*cis*-2-MCol	*trans*-2-MCol	CHone	MeO CHane	Phenol	CHol	Anisole	2-HCO	MeOH	
α-Al_2O_3	13.5	16.2	9.6	0.3	0.1	1.3	0.0	0.3	0.0	0.2	0.0	0.2	95.8
BN	6.5	8.1	3.2	0.5	0.3	0.1	0.0	0.1	0.0	0.0	0.2	0.0	96.2
H-ZSM-5	19.2	23.5	0.3	5.8	9.1	3.4	0.2	0.2	0.2	0.5	0.2	2.0	98.6
CeO_2	57.6	56.4	20.8	9.3	4.5	9.0	0.5	0.5	5.5	0.2	0.0	2.3	95.7
SiO_2	29.4	45.0	33.0	4.8	1.9	4.6	0.1	0.1	0.1	0.5	1.1	1.0	103.0
Nb_2O_5	43.6	13.6	6.0	1.3	0.6	0.6	0.2	0.2	0.1	0.2	0.3	0.2	96.2
TiO_2 (anatase)	24.4	40.6	29.6	3.6	2.1	2.0	0.1	0.1	0.2	0.1	0.1	0.4	97.9
TiO_2 (rutile)	15.3	15.3	7.2	1.1	0.5	1.0	0.3	0.3	0.1	0.5	0.4	0.2	96.1
TiO_2 (P-25)	17.4	33.3	24.0	2.3	1.0	2.0	0.2	0.2	0.1	0.3	0.3	0.4	97.4
Hydroxyapatite	21.4	10.4	7.3	0.5	0.2	0.4	0.0	0.1	0.2	0.0	0.0	0.1	98.4
Activated carbon	18.2	29.8	18.7	4.5	1.6	0.3	0.1	0.1	0.1	0.0	0.2	0.1	95.9
Carbon black	6.9	4.6	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	95.7

[a]Conditions: guaiacol (5 mmol), catalyst (Pd = 3 wt%, 100 mg), water (10 g), 373 K, H_2 (1 MPa at r.t.), 4 h.
2-MCO: 2-methoxycyclohexanone, 2-MCol: 2-methoxycyclohexanol, CHone: cyclohexanone, MeOH: methanol, MeOCHane: methoxycyclohexane, CHol: cyclohexanol, 2-HCO: 2-hydroxycyclohexanone.

[b]Dispersion (%) = $\left[\frac{\text{Amount of CO adsorption}}{\text{Total amount of Pd}}\right] \times 100$

Table S5. Product composition in the selective hydrogenation of guaiacol over Pd catalysts with various supports at similar conversion level.[a]

Support	Dispersion[b] [%]	Time [h]	Conv. [%]	Selectivity (C-based) [%] 2-MCO	*cis*-2-MCol	*trans*-2-MCol	CHone	MeOCHane	Phenol	CHol	Anisole	2-HCO	MeOH	Guaiacol conversion rate [mmol/(g_{Pd} • h)]	C. B. [%]
α-Al_2O_3	13.5	5	24.4	80.5	7.4	3.1	5.0	0.1	0.8	0.5	1.2	0.3	1.0	78	97.7
BN	6.5	9	19.9	67.6	16.6	10.2	1.9	0.3	0.9	0.4	0.3	1.2	0.7	30	95.7
CeO_2	57.6	1.5	21.3	49.2	10.8	5.6	20.2	0.1	2.3	6.6	0.5	0.2	4.4	288	104.6
SiO_2	29.4	2	25.9	70.2	8.8	3.6	8.8	1.7	0.6	0.3	2.0	2.2	1.8	223	100.8
Nb_2O_5	43.6	7	17.1	70.3	8.3	3.3	8.0	1.4	1.8	0.2	2.1	2.6	2.0	29	95.1
TiO_2 (anatase)	24.4	2	24.0	82.8	5.6	3.3	5.4	0.5	0.5	0.5	0.5	0.0	1.0	173	100.0
TiO_2 (rutile)	15.3	4	15.3	74.0	6.3	3.1	6.8	1.0	1.4	0.1	2.6	2.8	1.8	48	96.3
Hydroxyapatite	21.4	8	22.6	82.5	5.9	3.0	5.4	0.4	0.5	0.1	1.8	0.5	0.7	40	96.5
Activated carbon	18.2	3	23.0	70.8	16.7	6.8	1.7	0.3	0.1	0.3	0.0	2.8	0.4	107	96.0

[a]Conditions: guaiacol (5 mmol), catalyst (Pd = 3 wt%, 100 mg), water (10 g), 373 K, H_2 (1 MPa at r.t.).
2-MCO: 2-methoxycyclohexanone, 2-MCol: 2-methoxycyclohexanol, CHone: cyclohexanone, MeOH: methanol, MeOCHane: methoxycyclohexane, CHol: cyclohexanol, 2-HCO: 2-hydroxycyclohexanone.

[b]Dispersion (%) = $\left[\frac{\text{Amount of CO adsorption}}{\text{Total amount of Pd}}\right] \times 100$

Table S6. Time courses of selective hydrogenation of guaiacol over supported Pd catalysts.[a]

Catalyst	Time [h]	Conv. [%]	Yield (C-based) [%] 2-MCO	*cis*-2-MCol	*trans*-2-MCol	CHone	MeOCHane	Phenol	CHol	Anisole	2-HCO	MeOH	2-MCO sel. [%]	C.B. [%]
TiO_2 (anatase)	0	5.3	1.6	0.1	0.1	0.1	0.0	0.1	0.0	0.0	0.0	0.0	80.0	96.8
	2	24.0	16.8	1.1	0.7	1.1	0.1	0.1	0.1	0.1	0.0	0.2	82.8	96.4
	4	40.6	29.6	3.6	2.1	2.0	0.2	0.1	0.2	0.1	0.1	0.4	77.1	97.9
	6	53.5	42.3	5.0	2.7	3.0	0.4	0.1	0.5	0.1	0.1	0.6	77.2	101.1
	8	57.6	47.3	5.5	2.8	3.3	0.4	0.0	0.4	0.1	0.1	0.5	78.3	102.9
	12	71.0	55.6	8.0	3.9	3.3	0.5	0.1	0.7	0.1	0.1	0.7	76.2	102.0
	16	93.8	65.1	15.4	7.5	3.7	1.1	0.1	0.9	0.1	0.1	1.1	68.5	101.3
	20	96.6	56.9	21.8	10.5	4.3	1.0	0.1	1.7	0.0	0.0	1.0	58.5	100.8
	24	99.9	7.6	49.0	33.1	1.5	1.3	0.1	6.3	0.0	0.0	1.2	7.6	100.3
SiO_2	0	7.1	3.2	0.3	0.2	0.2	0.0	0.1	0.0	0.0	0.0	0.1	78.0	97.3
	2	31.1	22.6	2.5	1.1	2.5	0.5	0.1	0.1	0.6	0.6	0.5	72.7	99.8
	4	45.0	33.0	4.7	2.0	4.6	0.9	0.1	0.1	0.5	1.1	1.0	68.8	103.0
	6	67.0	49.7	7.7	3.5	6.2	1.4	0.1	0.4	0.3	1.4	1.2	69.1	104.8
	8	81.1	56.6	9.6	4.5	8.4	1.7	0.1	0.7	0.2	1.9	1.6	66.4	104.1
	10	95.4	59.8	12.3	7.1	8.9	1.9	0.1	1.6	0.1	1.9	2.0	62.5	100.3
	12	99.6	53.3	19.2	11.5	9.7	2.3	0.3	2.5	0.1	2.0	2.2	51.7	103.4
	16	99.8	22.8	36.5	24.2	5.7	2.3	0.9	6.3	0.0	0.9	2.3	22.4	102.1
Activated carbon	0	3.7	1.2	0.1	0.1	0.0	0.0	0.1	0.0	0.0	0.0	0.0	80.0	97.8
	4	29.8	18.7	4.5	1.6	0.3	0.0	0.1	0.1	0.0	0.2	0.1	73.0	95.9
	9	65.7	41.8	14.1	6.2	1.0	0.2	0.0	0.3	0.0	1.8	0.4	63.5	100.2
	13	83.2	47.9	23.0	10.9	1.5	0.5	0.0	0.7	0.0	2.5	0.7	54.6	104.3
	17	96.5	51.2	23.5	20.1	1.6	0.5	0.1	0.9	0.1	1.7	0.8	50.9	104.0
	20.5	97.5	33.7	37.9	20.1	1.7	0.7	0.3	1.7	0.0	2.0	0.9	34.0	101.5
	24	99.7	0.9	54.9	34.6	3.6	0.7	0.9	3.4	0.0	0.0	1.0	0.9	100.3

[a]Conditions: guaiacol (5 mmol), catalyst (Pd = 3 wt%, 100 mg), water (10 g), 373 K, H_2 (1 MPa at r.t.).
2-MCO: 2-methoxycyclohexanone, 2-MCol: 2-methoxycyclohexanol, CHone: cyclohexanone, MeOH: methanol, MeOCHane: methoxycyclohexane, CHol: cyclohexanol, 2-HCO: 2-hydroxycyclohexanone.

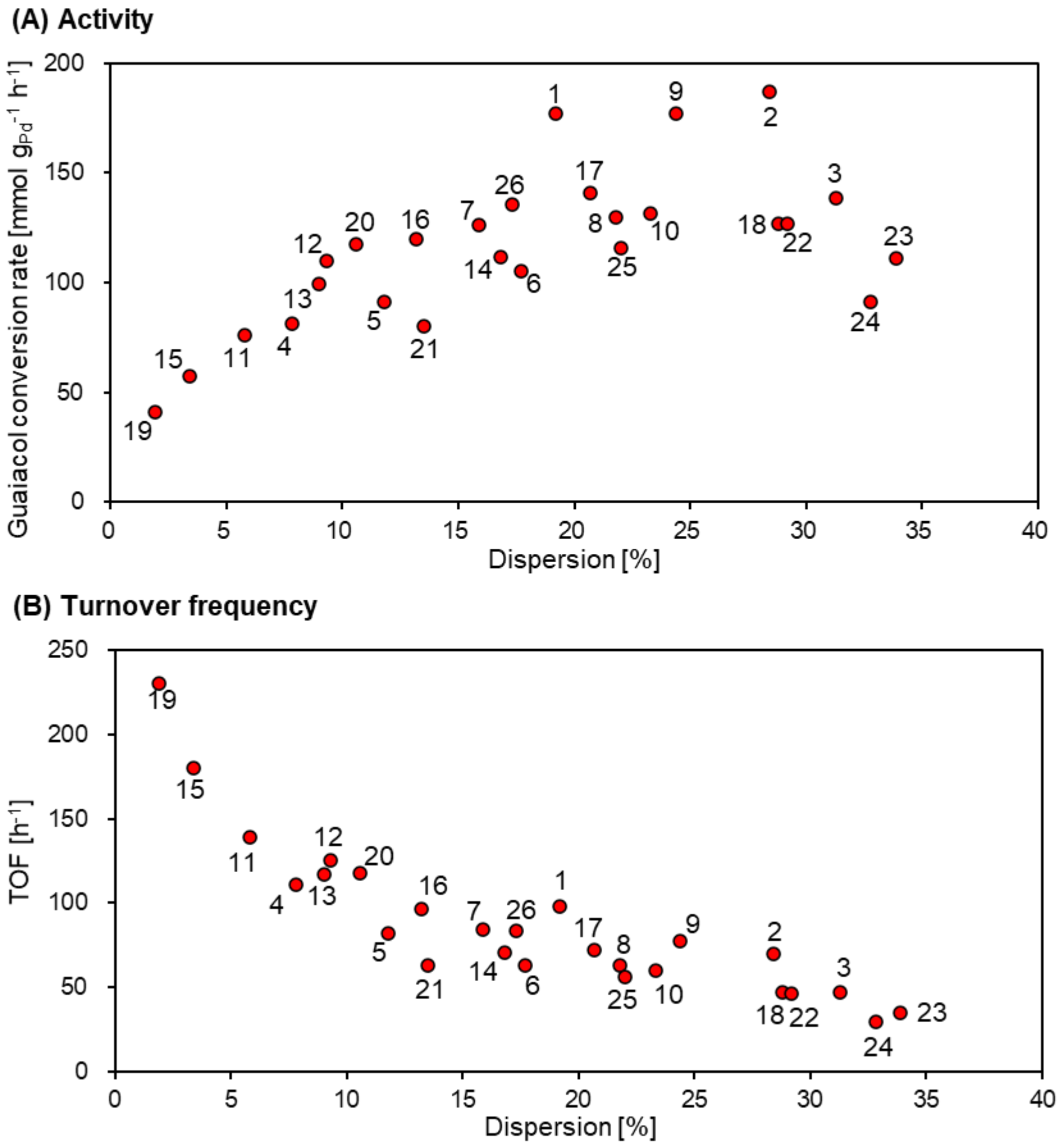


Figure S1. Correlation between Pd dispersion and catalytic activity for selective hydrogenation of guaiacol over Pd/TiO_2 catalyst.

All data involved in this figure are listed in Table S7.

Conditions: guaiacol (5 mmol), catalyst (100 mg), water (10 g), 373 K, H_2 (1 MPa at r.t.).

Table S7. Correlation between Pd dispersion and product selectivity for selective hydrogenation of guaiacol over Pd/TiO_2 catalyst.[a]

Entry	Pd loading [wt%]	Pd precursor	Calcination temp. [K]	D^b [%]	Time [h]	Conv. [%]	Yield (C-based) [%]										Guaiacol conv. rate [mmol/(g_{Pd} • h)]	C.B. [%]
							2-MCO	*cis*-2-MCol	*trans*-2-MCol	CHone	MeOCHane	Phenol	CHol	Anisole	2-HCO	MeOH		
1	5.1	Pd(acac)$_2$	573	19.2	1	19.8	14.5	1.0	0.6	1.0	0.1	0.1	0.1	0.1	0.1	0.1	177	97.8
2	2.9		573	28.4	2	22.7	17.8	1.3	0.6	1.2	0.1	0.1	0.1	0.1	0.0	0.3	187	99.0
3	1.0		573	31.3	8	23.5	17.4	1.3	0.7	1.4	0.2	0.1	0.1	0.1	0.0	0.3	138	98.2
4	5.5		773	7.8	2	16.6	15.0	0.9	0.5	0.8	0.1	0.1	0.0	0.2	0.1	0.2	81	101.2
5	2.7		773	11.8	4	22.0	15.2	1.3	0.9	1.0	0.1	0.1	0.0	0.1	0.1	0.2	91	97.0
6	1.0		773	17.7	8	20.5	13.7	0.7	0.4	1.0	0.0	0.1	0.0	0.2	0.1	0.2	105	96.0
7	9.1	Pd(OAc)$_2$	573	15.9	2	21.8	16.1	1.2	0.6	1.5	0.1	0.2	0.0	0.1	0.0	0.2	126	98.2
8	5.3		573	21.8	1.5	19.4	16.2	1.3	0.7	1.3	0.1	0.1	0.1	0.1	0.0	0.2	130	100.8
9	2.9		573	24.4	2	24.0	16.8	1.1	0.7	1.1	0.1	0.1	0.1	0.1	0.0	0.2	177	96.3
10	1.1		573	23.3	7	19.7	16.3	1.2	0.7	1.0	0.1	0.1	0.1	0.1	0.1	0.2	131	100.2
11	10.9		773	5.8	3	24.9	17.3	1.7	0.9	1.2	0.1	0.1	0.0	0.1	0.3	0.2	76	97.1
12	4.8		773	9.3	2	24.1	17.1	1.5	0.5	1.1	0.1	0.1	0.1	0.2	0.1	0.3	110	97.1
13	2.8		773	9.0	3	21.0	13.8	0.6	0.3	0.7	0.0	0.1	0.1	0.1	0.1	0.1	99	95.2
14	1.0		773	16.8	8	20.8	13.8	1.3	0.8	0.9	0.0	0.1	0.1	0.1	0.1	0.1	111	96.4
15	10.7	Pd(NO$_3$)$_2$	573	3.4	3	20.1	14.7	1.3	0.7	0.9	0.1	0.1	0.0	0.0	0.0	0.2	57	97.9
16	5.6		573	13.2	2	25.0	21.8	1.9	1.1	1.4	0.2	0.1	0.1	0.1	0.1	0.1	120	101.8
17	2.8		573	20.7	3	21.7	18.7	1.5	1.0	1.2	0.1	0.1	0.1	0.1	0.1	0.2	141	101.3
18	1.1		573	28.8	8	19.5	17.8	1.5	0.9	1.3	0.1	0.2	0.1	0.1	0.1	0.2	127	102.6
19	11.3		773	1.9	3	18.3	10.8	1.2	0.6	0.7	0.0	0.2	0.0	0.1	0.4	0.2	41	95.9
20	5.7		773	10.6	2	24.1	20.7	1.8	0.8	1.4	0.4	0.2	0.1	0.3	0.6	0.1	117	102.1
21	2.9		773	13.5	4	21.9	14.4	1.2	0.7	1.1	0.2	0.2	0.1	0.2	0.1	0.2	80	96.5
22	1.0		773	29.2	7	19.0	13.9	1.2	1.0	0.9	0.0	0.1	0.1	0.1	0.1	0.1	127	98.6
23	5.0	PdCl$_2$	573	33.9	2	21.7	16.0	1.1	0.4	2.0	0.1	0.2	0.1	0.2	1.4	0.6	111	100.3
24	4.9		773	32.8	2	19.1	12.3	0.6	0.4	2.0	0.1	0.1	0.1	0.2	1.5	0.2	91	98.4
25	4.7	Pd(NH$_3$)$_4$Cl$_2$	573	22.0	2	22.8	15.6	1.0	0.5	2.3	0.1	0.1	0.0	0.1	1.4	0.4	116	98.7
26	5.1		773	17.3	1.5	22.3	14.3	1.1	0.4	2.1	0.1	0.2	0.0	0.2	1.5	0.3	136	97.8

[a]Conditions: guaiacol (5 mmol), Pd/TiO_2 (100 mg), water (10 g), 373 K, H_2 (1 MPa at r.t.).
2-MCO: 2-methoxycyclohexanone, 2-MCol: 2-methoxycyclohexanol, CHone: cyclohexanone, MeOH: methanol, MeOCHane: methoxycyclohexane, CHol: cyclohexanol, 2-HCO: 2-hydroxycyclohexanone.

[b]Dispersion (%) = $\left[\frac{\text{Amount (mol) of adsorbed CO}}{\text{Total amount (mol) of Pd}}\right] \times 100$

Table S8. Effect of chloride ion on selective hydrogenation of guaiacol over Pd/TiO_2 catalyst.[a]

Entry	Time [h]	Additive	$n_{additive}/n_{Pd}$ [mol/mol]	Conv. [%]	Yield (C-based) [%]										2-MCO sel. [%]	C.B. [%]
					2-MCO	*cis*-2-MCol	*trans*-2-MCol	CHone	MeO CHane	Phenol	CHol	Anisole	2-HCO	MeOH		
1	4	H_2SO_4	1.7	42.3	31.2	4.8	2.1	1.6	0.1	0.1	1.6	0.1	0.1	0.2	75.4	99.1
2	4	HCl	1.3	50.0	35.1	4.1	1.5	5.0	0.8	0.1	5.0	0.1	0.8	0.2	69.9	100.2
3	4	HCl	3.3	61.3	38.2	3.5	2.0	8.0	0.9	0.1	8.0	0.2	0.9	0.3	63.6	98.8
4	4	None	0.0	40.6	29.6	3.6	2.1	2.0	0.2	0.1	2.0	0.1	0.2	0.2	76.1	98.3
5	8	None	0.0	57.6	47.3	5.5	2.8	3.3	0.4	0.0	0.4	0.1	0.1	0.5	78.3	102.9
6	12	None	0.0	71.0	55.6	8.0	3.9	3.3	0.5	0.1	0.7	0.1	0.1	0.7	76.2	102.0

[a]Conditions: guaiacol (5 mmol), Pd/TiO_2 (Pd = 3 wt%, 100 mg), water (10 g), additive (shown in table), 373 K, H_2 (1 MPa at r.t.).
2-MCO: 2-methoxycyclohexanone, 2-MCol: 2-methoxycyclohexanol, CHone: cyclohexanone, MeOH: methanol, MeOCHane: methoxycyclohexane, CHol: cyclohexanol, 2-HCO: 2-hydroxycyclohexanone.

Table S9. Effect of solvent on selective hydrogenation of guaiacol and 2-methoxycyclohexanone over Pd/TiO_2 catalyst.[a, b]

Entry	Substrate	Solvent	$W_{catalyst}$ [g]	Conv. [%]	Yield (C-based) [%]										2-MCO sel. [%]	C.B. [%]
					2-MCO	*cis*-2-MCol	*trans*-2-MCol	CHone	MeOCHane	Phenol	CHol	Anisole	2-HCO	MeOH		
1	Guaiacol[a]	Water	0.1	40.6	29.6	3.6	2.1	2.0	0.2	0.1	0.2	0.1	0.1	0.4	77.1	97.9
2		Methanol	0.1	1.5	0.0	0.1	0.0	0.0	0.0	0.1	0.0	0.0	0.0	-	0.0	98.7
3		Ethanol	0.1	8.4	4.1	0.8	0.4	0.3	0.0	0.2	0.1	0.0	0.0	0.1	68.3	97.6
4		2-Propanol	0.1	1.5	0.4	0.1	0.0	0.0	0.0	0.1	0.0	0.0	0.1	0.0	57.1	99.2
5		Tetrahydrofuran	0.1	7.2	3.2	1.2	0.6	0.5	0.0	0.4	0.6	0.1	0.0	0.2	47.1	99.7
6		Cyclohexane	0.1	12.7	7.2	2.2	1.1	0.8	0.0	0.0	0.3	0.1	0.0	0.1	61.0	99.2
7		Dodecane	0.1	14.9	6.1	1.9	1.0	0.4	0.0	0.0	0.2	0.1	0.0	0.0	62.9	95.9
8			0.3	38.0	17.1	9.6	5.6	1.4	0.0	0.0	1.1	0.1	0.0	0.2	48.7	97.1
9		No solvent	0.1	13.9	6.9	2.0	1.0	0.4	0.1	0.0	0.2	0.1	0.0	0.0	64.5	96.7
10	2-MCO[b]	Water	0.1	53.7	-	28.2	25.5	0.2	0.1	0.0	0.1	0.0	0.0	0.5	-	101.4
11		Ethanol	0.1	34.4	-	19.2	18.1	0.4	0.0	0.0	0.0	0.0	0.0	0.0	-	103.3
12		Dodecane	0.1	76.2	-	49.1	24.8	0.3	0.8	0.0	0.0	0.0	0.0	1.1	-	100.0
13		No solvent	0.1	81.9	-	45.4	33.7	0.9	0.0	0.0	0.0	0.0	0.0	0.3	-	98.4

[a]Conditions(guaiacol): guaiacol (5 mmol), Pd/TiO_2 (Pd = 3 wt%, 100 mg), solvent (10 g), 373 K, H_2 (1 MPa at r.t.), 4 h.
[b]Conditions(2-MCO) : 2-MCO (2 mmol), Pd/TiO_2 (Pd = 3 wt%, 100 mg), solvent (10 g), 373 K, H_2 (1 MPa at r.t.), 2 h.
2-MCO: 2-methoxycyclohexanone, 2-MCol: 2-methoxycyclohexanol, CHone: cyclohexanone, MeOH: methanol, MeOCHane: methoxycyclohexane, CHol: cyclohexanol, 2-HCO: 2-hydroxycyclohexanone.

Table S10. Effect of solvent and substrate concentration on selective hydrogenation of guaiacol over Pd/TiO_2 catalyst.[a]

Entry	Solvent	Guaiacol conc. [mM]	Reaction time [h]	Conv. [%]	Yield (C based) [%]									C.B. [%]	Converted substrate amount [mmol g_{Pd}^{-1}]	Conversion rate [mmol g_{Pd}^{-1} h^{-1}]
					2-MCO	2-MCol	CHone	MeO CHane	Phenol	CHol	Anisole	2-HCO	MeOH			
1	Water	207	0	9.9	5.7	0.5	0.5	0.0	0.3	0.0	0.1	0.1	0.1	97.4	50.3	241
2		209	0.08	9.3	7.9	0.7	0.9	0.0	0.3	0.0	0.1	0.0	0.2	100.8	69.5	
3		200	0.25	15.8	12.9	0.9	1.7	0.0	0.2	0.0	0.2	0.0	0.3	99.5	110.6	
4		507	0	5.5	1.6	0.2	0.1	0.0	0.1	0.1	0.0	0.1	0.1	96.8	39.1	192
5		501	0.25	8.8	4.5	0.3	0.2	0.0	0.0	0.0	0.0	0.0	0.1	96.7	85.1	
6		512	0.50	11.3	6.8	0.4	0.3	0.0	0.2	0.0	0.1	0.0	0.1	96.9	135.2	
7		801	0	1.5	0.8	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.1	99.6	26.5	180
8		801	0.5	6.2	3.7	0.5	0.3	0.0	0.1	0.0	0.1	0.0	0.1	98.6	128.5	
9		809	1	8.7	6.2	0.7	0.5	0.0	0.1	0.0	0.1	0.0	0.1	99.0	206.3	
10		1611	0	0.9	0.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	99.7	21.5	193
11		1635	1	4.7	3.1	0.3	0.2	0.0	0.1	0.0	0.0	0.0	0.0	99.2	201.1	
12		1624	2	6.0	6.0	0.7	0.5	0.0	0.1	0.0	0.1	0.0	0.1	101.5	408.1	
13	Dodecane	203	0	1.5	1.6	1.1	0.3	0.0	0.0	0.0	0.0	0.0	0.0	101.5	20.1	62.3
14		208	0.5	9.1	4.0	2.4	0.6	0.0	0.0	0.2	0.1	0.0	0.0	98.3	50.4	
15		201	1	15.3	6.5	4.0	1.1	0.0	0.0	0.6	0.1	0.0	0.1	97.1	82.4	
16		512	0	3.6	0.6	0.2	0.1	0.0	0.0	0.0	0.0	0.0	0.0	97.3	15.2	55.0
17		507	2	6.5	4.7	2.2	0.5	0.0	0.0	0.2	0.1	0.0	0.0	101.3	128.8	
18		511	4	14.9	8.1	4.4	1.0	0.0	0.0	0.2	0.1	0.0	0.0	100.0	235.3	
19		816	0	1.3	0.4	0.1	0.0	0.0	0.0	0.0	0.5	0.0	0.0	99.8	27.1	50.4
20		822	3	8.0	4.0	1.7	0.3	0.0	0.0	0.1	0.1	0.0	0.0	98.2	170.0	
21		822	5	14.5	5.8	3.2	0.7	0.0	0.0	0.3	0.1	0.0	0.1	95.8	280.1	

Entry	Solvent	Guaiacol conc. [mM]	Reaction time [h]	Conv. [%]	Yield (C based) [%]									C.B. [%]	Converted substrate amount [mmol g_{Pd}^{-1}]	Conversion rate [mmol g_{Pd}^{-1} h^{-1}]
					2-MCO	2-MCol	CHone	MeO CHane	Phenol	CHol	Anisole	2-HCO	MeOH			
22	Ethanol	205	0	0.3	0.5	0.1	0.0	0.0	0.1	0.0	0.0	0.0	0.1	100.6	5.4	20.7
23		199	2	6.1	4.5	2.0	0.5	0.0	0.2	0.2	0.0	0.0	0.1	101.4	49.2	
24		201	4	13.9	8.0	4.2	0.6	0.0	0.1	0.3	0.0	0.0	0.1	99.4	99.2	
25		503	0	5.0	0.3	0.1	0.0	0.0	0.1	0.0	0.0	0.0	0.1	95.6	10.1	25.5
26		519	4	8.4	4.1	0.8	0.4	0.3	0.0	0.2	0.1	0.0	0.1	97.6	103.1	
27		503	8	14.6	7.8	2.6	1.2	0.5	0.0	0.2	0.2	0.0	0.1	98.4	213.8	
28		812	0	-0.3	0.2	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.0	100.6	8.1	33.0
29		820	4	5.5	3.6	1.3	0.1	0.0	0.1	0.1	0.0	0.0	0.0	99.7	140.7	
30		841	8	9.2	6.4	2.7	0.3	0.0	0.1	0.1	0.0	0.0	0.1	100.7	272.3	
31		1651	0	-2.9	0.1	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.0	103.1	10.9	43.0
32		1638	6	1.5	3.2	1.1	0.1	0.0	0.1	0.1	0.0	0.0	0.1	103.1	255.3	
33		1628	12	6.5	6.5	2.6	0.3	0.0	0.1	0.1	0.0	0.0	0.1	103.3	526.4	

[a]Conditions: guaiacol (2-10 mmol), Pd/TiO_2 (Pd = 3 wt%, 100 mg), solvent (10 g), 373 K, H_2 (1 MPa at r.t.).
2-MCO: 2-methoxycyclohexanone, 2-MCol: 2-methoxycyclohexanol, CHone: cyclohexanone, MeOH: methanol, MeOCHane: Methoxycyclohexane, CHol: cyclohexanol, 2-HCO: 2-hydroxycyclohexanone.

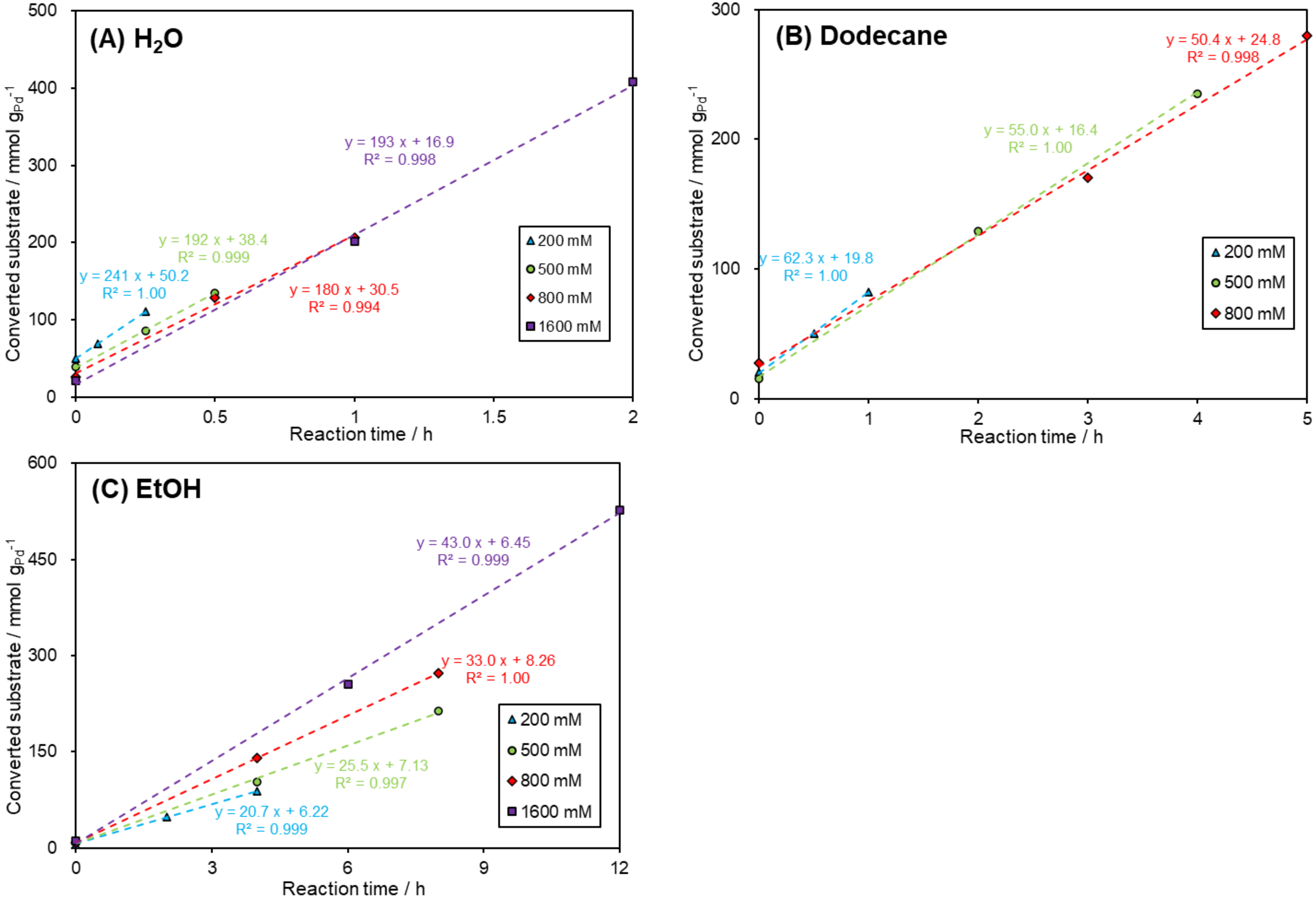


Figure S2. Effect of solvent and substrate concentration on selective hydrogenation of guaiacol over Pd/TiO_2 catalyst. Conditions: guaiacol (2-16 mmol), Pd/TiO_2 (Pd =3 wt%, 100 mg), solvent (10 g), H_2 (1 MPa at r.t.), 373 K.

Table S11. Effects of reaction temperature and hydrogen pressure on selective hydrogenation of guaiacol over Pd/TiO_2 catalyst.[a]

Entry	Temp. [K]	P_{H2} [MPa]	Time [h]	Conv. [%]	Yield (C-based) [%]										2-MCO sel. [%]	C.B. [%]
					2-MCO	*cis*-2-MCol	*trans*-2-MCol	CHone	MeO CHane	Phenol	CHol	Anisole	2-HCO	MeOH		
1	353	1	10	41.0	29.3	2.3	1.1	1.3	0.1	0.0	0.1	0.1	0.0	0.3	84.7	96.5
2			48	70.5	42.5	17.1	8.7	2.1	0.6	0.2	1.5	0.1	0.0	0.5	58.0	102.8
3	373	1	4	40.6	29.6	3.6	2.1	2.0	0.2	0.1	0.2	0.1	0.1	0.4	77.1	97.9
4			12	71.0	55.6	8.0	3.9	3.3	0.5	0.1	0.7	0.1	0.1	0.7	76.2	102.0
5	393	1	1.5	42.3	32.1	2.7	1.4	3.0	0.2	0.2	0.2	0.3	0.1	0.5	78.9	98.4
6			3	81.2	55.0	9.4	5.1	6.8	0.7	0.1	0.8	0.3	0.2	1.3	69.0	98.4
7	373	0.1	4	21.9	13.9	0.8	0.4	1.2	0.1	0.1	0.0	0.1	0.0	0.2	82.7	95.0
8			6	41.5	27.0	3.3	1.8	2.0	0.2	0.1	0.3	0.1	0.1	0.4	76.5	93.7
9		1	4	40.6	29.6	3.6	2.1	2.0	0.2	0.1	0.2	0.1	0.1	0.4	77.1	97.9
10		3	4	45.2	28.3	5.1	2.8	1.8	0.2	0.1	0.3	0.1	0.1	0.3	72.4	94.0
11		5	4	43.1	26.9	6.4	3.4	1.6	0.2	0.1	0.4	0.1	0.0	0.3	68.3	96.3

[a]Conditions: guaiacol (5 mmol), catalyst (Pd = 3 wt%, 100 mg), water (10 g).
2-MCO: 2-methoxycyclohexanone, 2-MCol: 2-methoxycyclohexanol, CHone: cyclohexanone, MeOH: methanol, MeOCHane: methoxycyclohexane, CHol: cyclohexanol, 2-HCO: 2-hydroxycyclohexanone.

Table S12. Reusability of Pd/TiO_2 catalyst in selective hydrogenation of guaiacol.[a]

Entry	Regeneration method	Number of catalyst use	Conv. [%]	Yield (C-based) [%]										2-MCO sel. [%]	C.B. [%]
				2-MCO	*cis*-2-MCol	*trans*-2-MCol	CHone	MeO Chane	Phenol	CHol	Anisole	2-HCO	MeOH		
1	Washing with water	1	64.7	47.1	8.3	4.1	3.9	0.6	0.1	0.7	0.2	0.1	0.7	71.6	101.1
2		2	57.0	43.6	5.4	2.7	3.5	0.6	0.1	0.3	0.2	0.3	0.6	76.1	100.3
3		3	37.0	26.2	2.1	0.9	2.2	0.2	0.1	0.1	0.1	0.1	0.4	80.9	95.4
4	Calcination at 573 K	1	63.5	48.2	7.3	3.9	3.7	0.5	0.1	0.6	0.1	0.0	0.6	74.2	101.5
5		2	55.1	44.3	5.9	3.1	3.3	0.5	0.1	0.4	0.1	0.1	0.6	75.9	103.1
6		3	42.8	33.4	3.9	2.0	2.8	0.2	0.2	0.1	0.2	0.1	0.5	77.0	100.6
7	Washing with toluene	1	62.9	45.6	7.1	3.6	3.8	0.6	0.1	0.5	0.2	0.1	0.6	73.3	99.3
8		2	69.5	50.3	7.9	3.9	4.6	0.8	0.1	0.5	0.2	0.3	0.9	72.4	100.0
9		3	64.0	47.4	6.8	3.3	4.7	0.9	0.1	0.4	0.2	0.5	1	72.6	101.3

[a]Conditions: guaiacol (5 mmol), catalyst (Pd = 3 wt%, 200 mg), water (10 g), 373 K, H_2 (1 MPa at r.t.), 4 h.
2-MCO: 2-methoxycyclohexanone, 2-MCol: 2-methoxycyclohexanol, CHone: cyclohexanone, MeOH: methanol, MeOCHane: methoxycyclohexane, CHol: cyclohexanol, 2-HCO: 2-hydroxycyclohexanone.

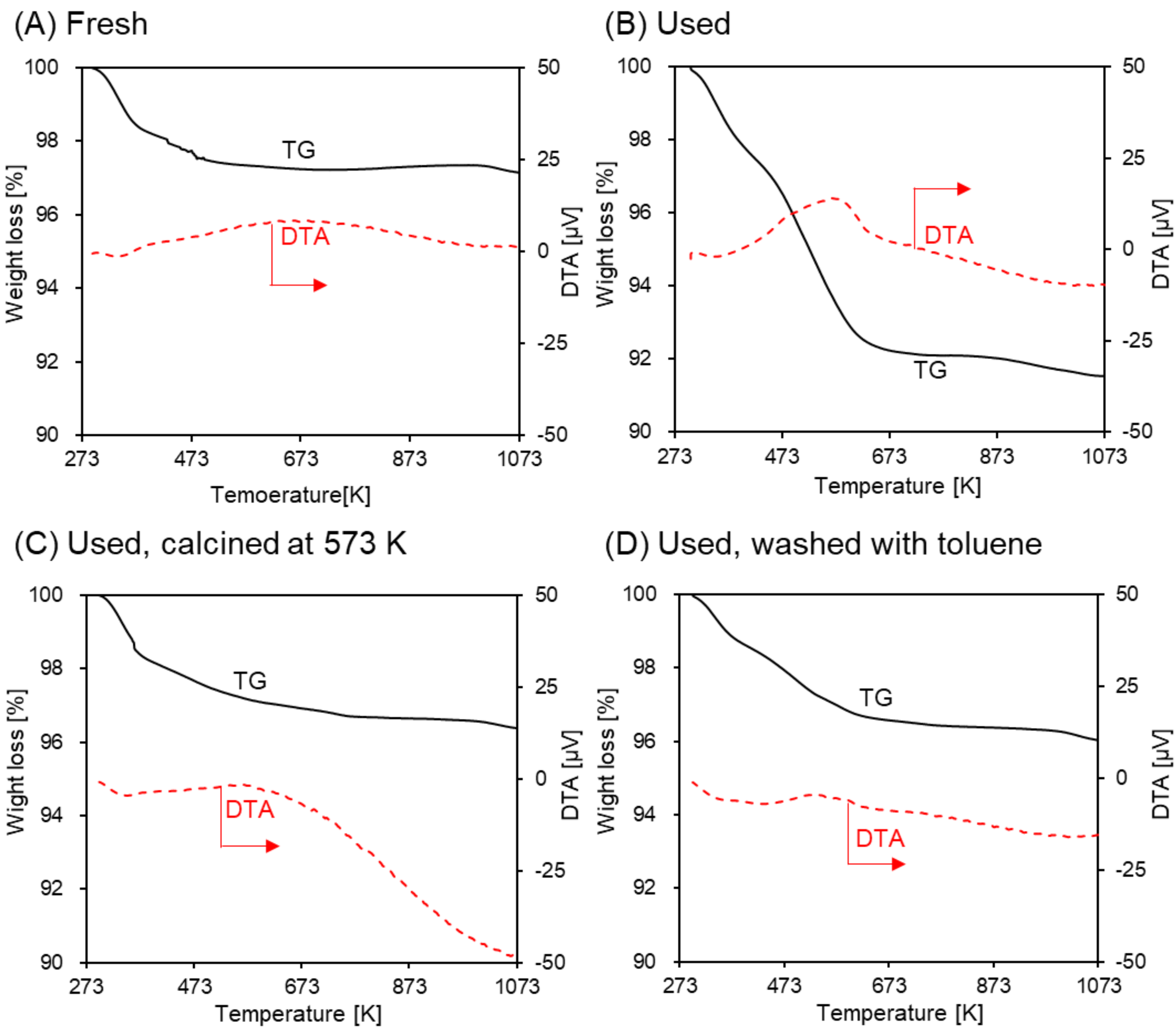


Figure S3. TG-DTA profiles for Pd/TiO_2 catalysts.

Reaction conditions: guaiacol (5 mmol), Pd/TiO_2 (Pd = 3 wt%, 200 mg), water (10 g), 373 K, H_2 (1 MPa at r.t.), 4 h.

Measurement conditions: 10 mg sample heated from room temperature to 1073 K under an air flow of 30 mL min^{-1} at a ramp rate of 10 K min^{-1}.

(A) The fresh catalyst was washed with water and dried at 383 K for 12 h.

(B) The used catalyst was washed with water and dried at 383 K for 12 h.

(C) The used catalyst was washed with water, dried at 383 K for 12 h and calcined at 573 K for 3 h.

(D) The used catalyst was washed with water and toluene and dried at 383 K for 12 h.

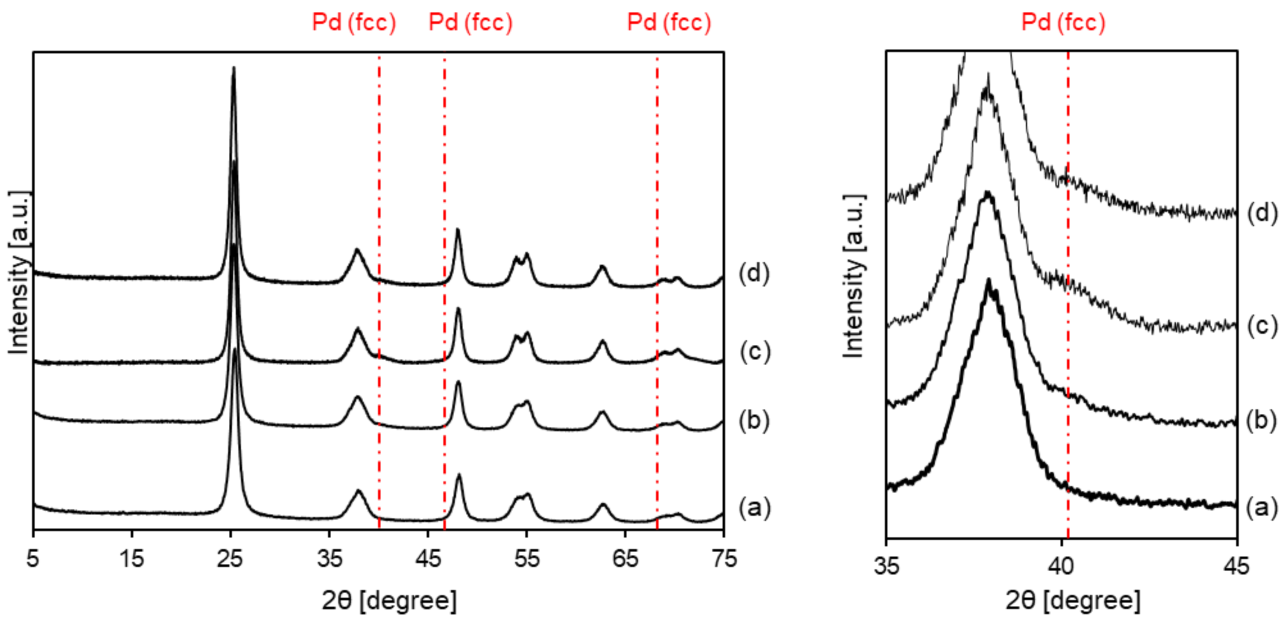


Figure S4. XRD patterns of Pd/TiO_2 catalysts after reuse.

Reaction conditions: guaiacol (5 mmol), Pd/TiO_2 (Pd = 3 wt%, 200 mg), water (10 g), 373 K, H_2 (1 MPa at r.t.), 4 h.

Measured after liquid phase reduction (373 K) and dried at 383 K for 12 h.

Pd (fcc) was referred to ICSD (52251).

(a) Anatase TiO_2 calcined at 573 K for 3 h.

(b) The fresh catalyst

(c) The twice used catalyst: regenerated by calcination at 573 K.

(d) The twice used catalyst: regenerated by washing toluene.

Table S13. Change of Pd dispersion by catalyst regeneration of calcination at 573 K.[a]

Number of catalyst use	Dispersion [%]
1	24.4
2	22.4
3	14.9

[a]Reaction conditions: guaiacol (5 mmol), Pd/TiO_2 (Pd = 3 wt%, 200 mg), water (10 g), 373 K, H_2 (1 MPa at r.t.), 4 h.

Regeneration method: washing by water and dried at 383 K for 12 h, calcined at 573 K for 3 h.

$$\text{Dispersion (\%)} = \left[\frac{\text{Amount (mol) of adsorbed CO}}{\text{Total amount (mol) of Pd}}\right] \times 100$$

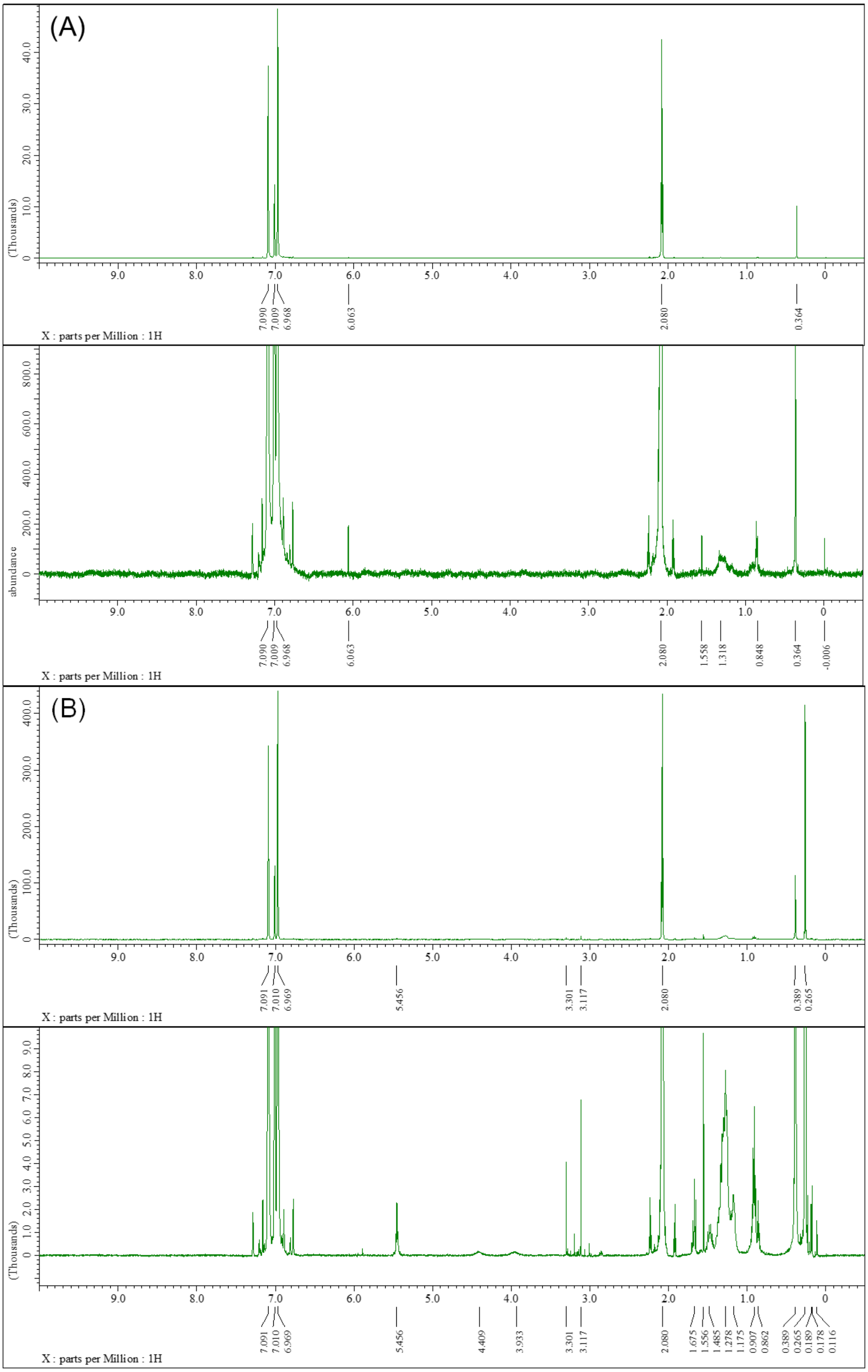


Figure S5. ^{1}H NMR spectra of organic species extracted from the used catalyst with toluene-d_8:

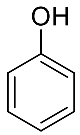
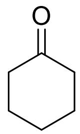
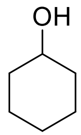
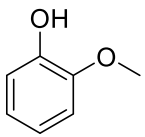
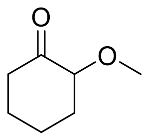
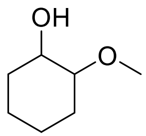
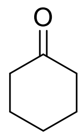
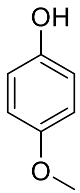
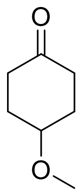
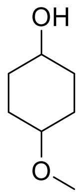
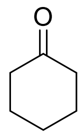
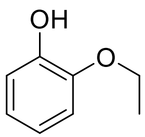
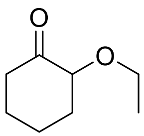
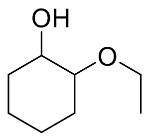
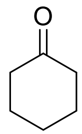
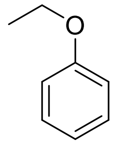
for the figure A and B, the upper and bottom spectra represent the whole range and expanded ones.

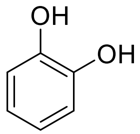
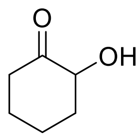
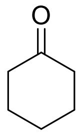
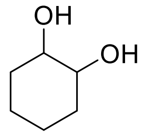
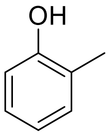
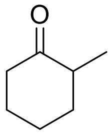
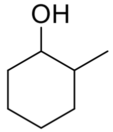
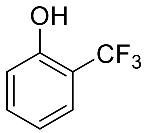
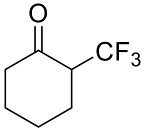
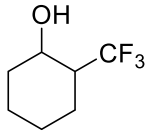
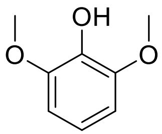
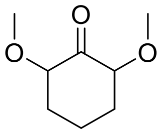
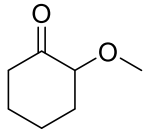
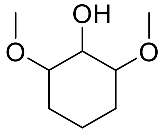
(A)Toluene-d_8 (as a reference) (B) Organic species extracted from the used catalyst with toluene-d_8

Spectrum B: After the reaction, the used catalyst (0.3 g) collected by filtration, washed with water (30 g), and dried at 383 K overnight, the organic species were extracted with 2 mL of toluene-d_8.

Reaction conditions: guaiacol (5 mmol), Pd/TiO_2 (Pd = 3 wt%, 200 mg), water (10 g), 373 K, H_2 (1 MPa at r.t.), 4 h.

Table S14. Substrate scope of Pd/TiO_2 catalyst.[a]

Substrate	Time [h]	Conv. [%]	Yield of each product (C based) [%]							
	0	15.7		15.8		n.d.				
	0.25	27.5		27.6		n.d.				
	0.50	49.5		50.3		n.d.				
	1	99.4		86.6		7.5				
	2.5	99.8		77.9		27.4				
	0	5.5		1.6		0.2		0.1	Others[b]	0.4
	0.25	8.5		4.5		0.3		0.2		0.0
	0.50	11.3		6.8		0.4		0.3		0.4
	4	40.6		29.6		5.7		2.0		1.2
	16	93.8		65.1		22.9		3.7		2.5
	0	12.2		11.1		0.2		0.2	Others[c]	0.2
	0.25	23.2		19.5		0.2		0.6		0.3
	0.50	36.8		37.1		0.5		1.5		0.3
	1	75.4		74.3		1.6		2.4		0.8
	1.5	90.9		90.2		2.2		3.9		0.7
	2	96.2		90.5		2.7		4.2		0.3
	4	99.8		29.5		72.8		2.4		1.9
	0	4.3		1.6		0.1		0.0		0.1
	0.25	7.7		3.3		0.3		0.2		0.1
	0.50	12.2		6.3		0.6		0.3		0.2
	4	37.4		26.8		3.4		1.6		0.3
	16	92.9		51.3		27.6		3.9		0.8

Substrate	Time [h]	Conv. [%]	Yield of each product (C based) [%]							
	0	8.4		8.7		0.3		n.d.		
	0.25	27.1		20.9		1.2		n.d.		
	0.5	43.7		46.5		2.3		n.d.		
	1	64.1		55.1		3.7		0.5		
	2	94.6		87.0		6.7		5.5		
	0	10.6		6.0		n.d.				
	0.25	21.2		18.6		0.2				
	0.50	35.8		32.3		0.3				
	2	67.0		59.9		1.0				
	4	93.9		83.2		4.3				
	0	10.0		5.9		1.8				
	0.25	23.2		16.5		5.1				
	0.50	35.5		26.2		6.9				
	4	96.2		83.2		11.8				
	0.5	4.2		0.1		0.3		0.1	Others[d]	0.3
	6	9.8		1.1		2.1		0.8		2.5
	11	13.8		2.4		2.4		1.4		4.2
	24	28.8		7.4		6.5		5.7		10.0

[a]Conditions: substrate (5 mmol), Pd/TiO_2 (Pd = 3 wt%, 100 mg), water (10 g), 373 K, H_2 (1 MPa at r.t.).

n.d.: not detected.

b (guaiacol): others include methanol, cyclohexanol, phenol, anisole, methoxycyclohexane, 2-hydroxycyclohexanone.
c (4-methoxyphenol): others include methanol, cyclohexanol, and 1,4-cyclohexanediol.
d (syringol): others include methanol, 2-methoxycyclohexanol, 2-hydroxycyclohexanone, 1,2-cyclohexanediol.

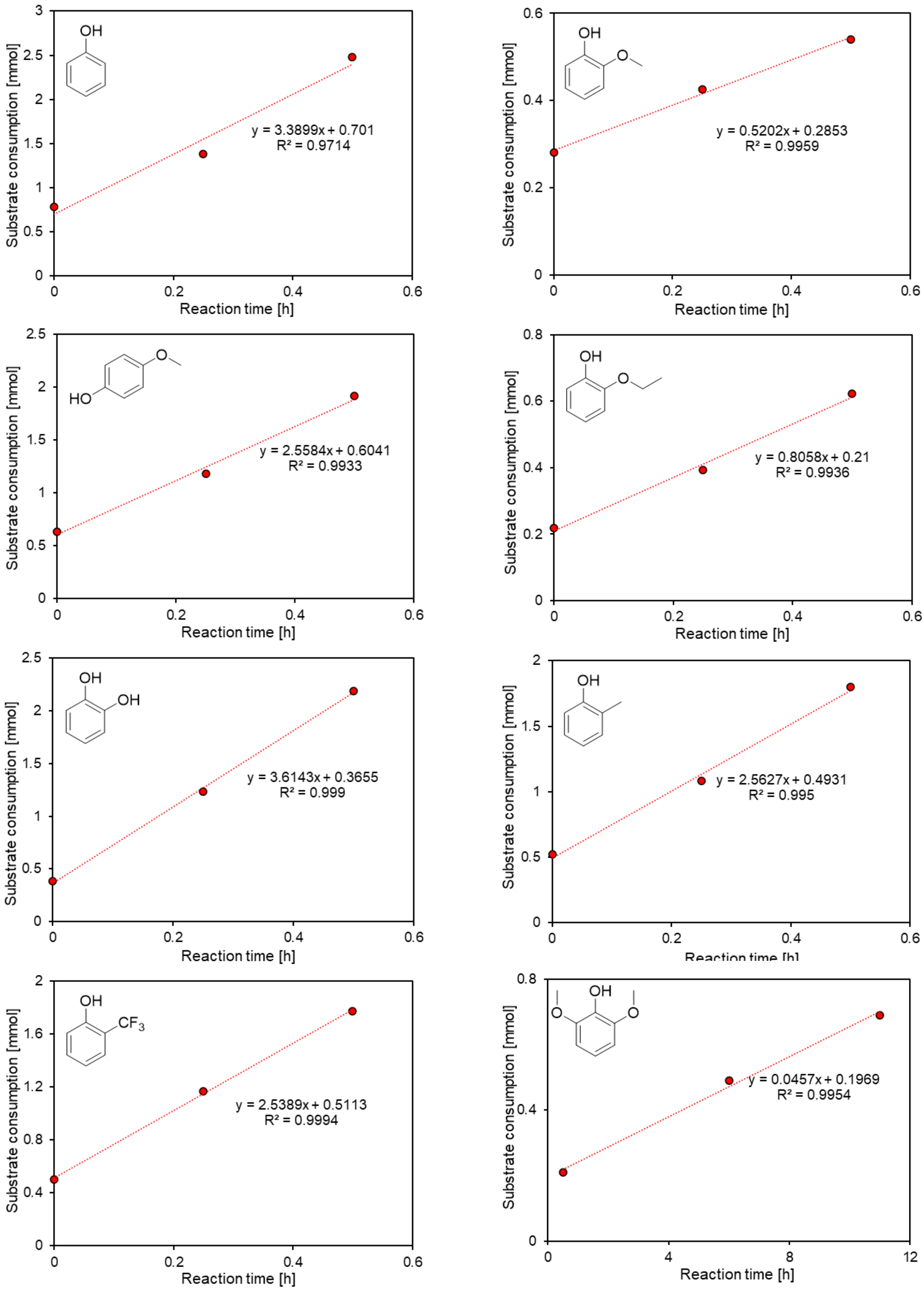


Figure S6. Initial reaction rate of selective hydrogenation of each substrate over Pd/TiO_2 catalyst.
Conditions: substrate (5 mmol), Pd/TiO_2 (Pd = 3 wt%, 100 mg), water (1 0 g), 373 K, H_2 (1 MPa at r.t.)

Table S15. Hydrogenation of guaiacol and 2-methoxycyclohexanone (2-MCO) over Pd/TiO_2 catalyst.[a]

Entry	Substrate	Time [h]	Conv. [%]	Yield (C-based) [%]										*cis*/*trans* ratio of 2-MCol [mol/mol]	C.B. [%]
				2-MCO	*cis*-2-MCol	*trans*-2-MCol	CHone	MeO CHane	Phenol	CHol	Anisole	2-HCO	MeOH		
1	Guaiacol (5 mmol)	4	40.6	29.6	3.6	2.1	2.0	0.2	0.1	2.0	0.1	0.2	0.2	1.7	98.3
2		8	57.6	47.3	5.5	2.8	3.3	0.4	0.0	0.4	0.1	0.1	0.5	2.0	102.9
3		12	71.0	55.6	8.0	3.9	3.3	0.5	0.1	0.7	0.1	0.1	0.7	2.1	102.0
4		24	99.9	7.6	49.0	33.1	1.5	1.3	0.1	6.3	0.0	0.0	1.2	1.5	100.3
5	2-MCO (2 mmol)	1	38.9	-	18.9	18.5	0.2	0.0	0.0	0.1	0.0	0.0	0.5	1.0	99.3
6		2	53.7	-	28.2	25.5	0.2	0.1	0.0	0.1	0.0	0.0	0.5	1.1	101.4
7		6	81.7	-	46.3	38.2	0.2	0.1	0.0	0.2	0.0	0.0	0.6	1.2	103.9

[a]Conditions for guaiacol: guaiacol (5 mmol), water (10 g), Pd/TiO_2 (Pd = 3 wt%, 100 mg), H_2 (1 MPa at r.t.), 373 K.
Conditions for 2-MCO: 2-MCO (2 mmol), water (10 g), Pd/TiO_2 (Pd = 3 wt%, 50 mg), H_2 (1 MPa at r.t.), 373 K.

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