Electronic Supplementary information for

Dual Pd^{2+} and Pd^{0} Sites on CeO_2 for Selective Oxidative C-C Bond Breaking of β-O-4 Linkage in Lignin

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1. Characterization and Equipment

Transmission electron microscope (TEM) and high-resolution transmission electron microscope (HR-TEM) were used to examine the morphology of the catalysts on JEM-2100F electron microscope. X-ray diffraction (XRD) analysis was conducted using a Philips X'Pert Pro diffractometer (PW3040/60) with Cu Kα radiation (λ = 1.542 Å) at 40 kV and 40 mA. The diffraction patterns were recorded at a scanning rate of 2°/min over a range of 5° to 80°. Elemental analysis was performed using an Atom Scan 16 inductively coupled plasma atomic emission spectrometer (ICP-AES). The samples were dissolved in a known amount of aqua regia before measurement to ensure that the concentrations of the measured elements were comparable to those of the prepared standard solutions. X-ray photoelectron spectra (XPS) was used to analyze the surface chemical states of Pd, Ce and O with a Thermo Fisher XPS spectrometer (Escalab250Xi) using Al Kα radiation. The C1s peak at 284.6 eV was used as a reference for calibrating the binding energy. Raman spectra were obtained by exciting the sample at 532 nm with a Raman microscope system (LabRAM HR800, HORIBA Jobin Yvon) within the spectral range of 200 to 1000 cm^{-1} and a spectral resolution of 2 cm^{-1}. Gas chromatography-flame ionization detector (GC-FID, GC-2010 Pro A) was used to determine the conversion and product yields. 1 μL injection volume was used with a 30 m × 250 μm × 0.25 μm column (Rtx-SH-5), with a split ratio of 30:1. The GC conditions included an inlet temperature of 280 °C and an oven temperature program starting at 80 °C, ramping at 10 ^{o}C min−1 to 280 °C, resulting in a total run time of 32 minutes.

2. Figures and Tables

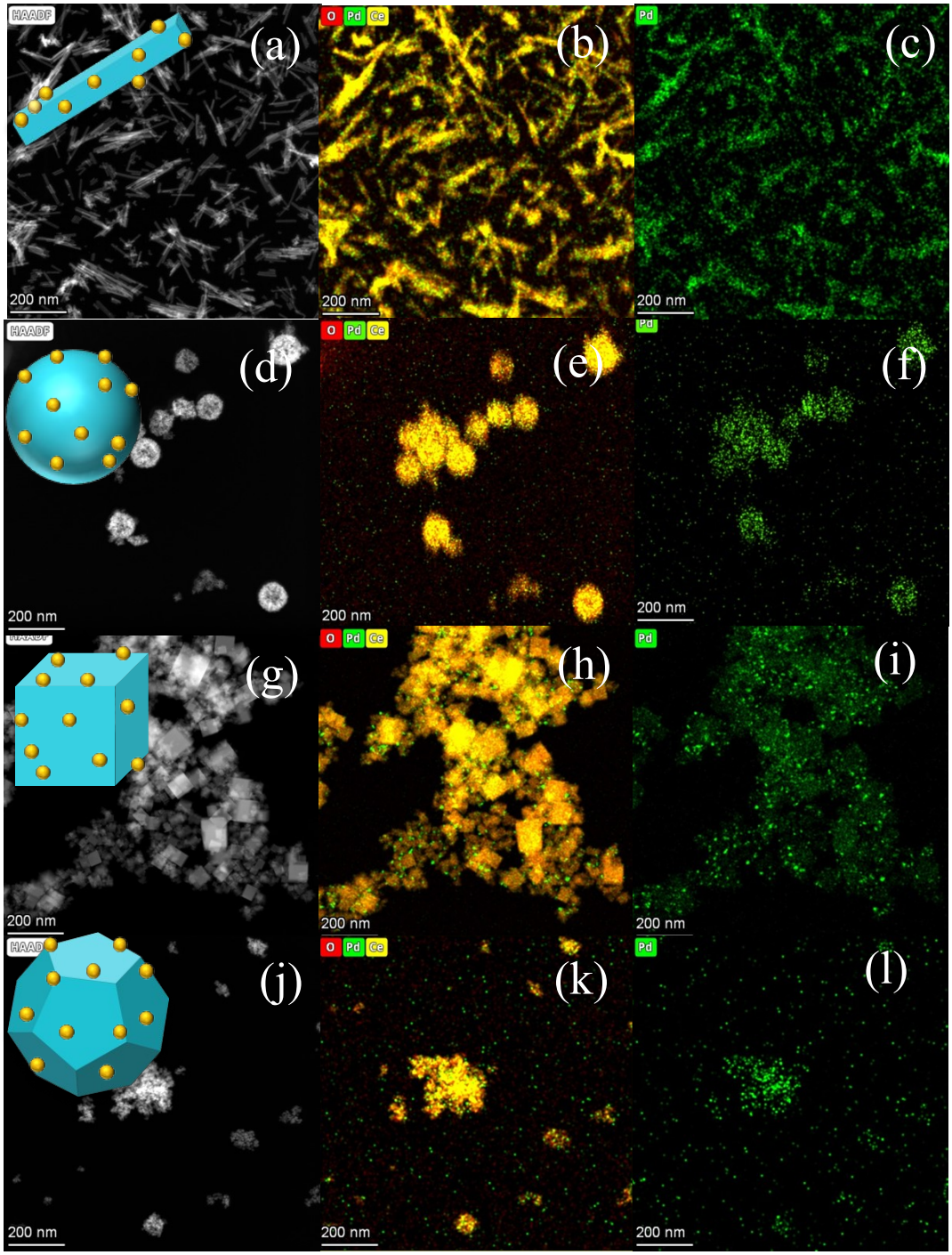

Fig. S1 HAADF-STEM images and corresponding EDS elemental mappings of all the Pd/CeO_2 catalysts with different morphologies: (a)-(c) Pd/CeO_2-R; (d)-(f) Pd/CeO_2-S; (g)-(i) Pd/CeO_2-C; (j)-(l) Pd/CeO2-P, respectively. Ce, O, and Pd elements are presented in yellow, red and green, respectively.

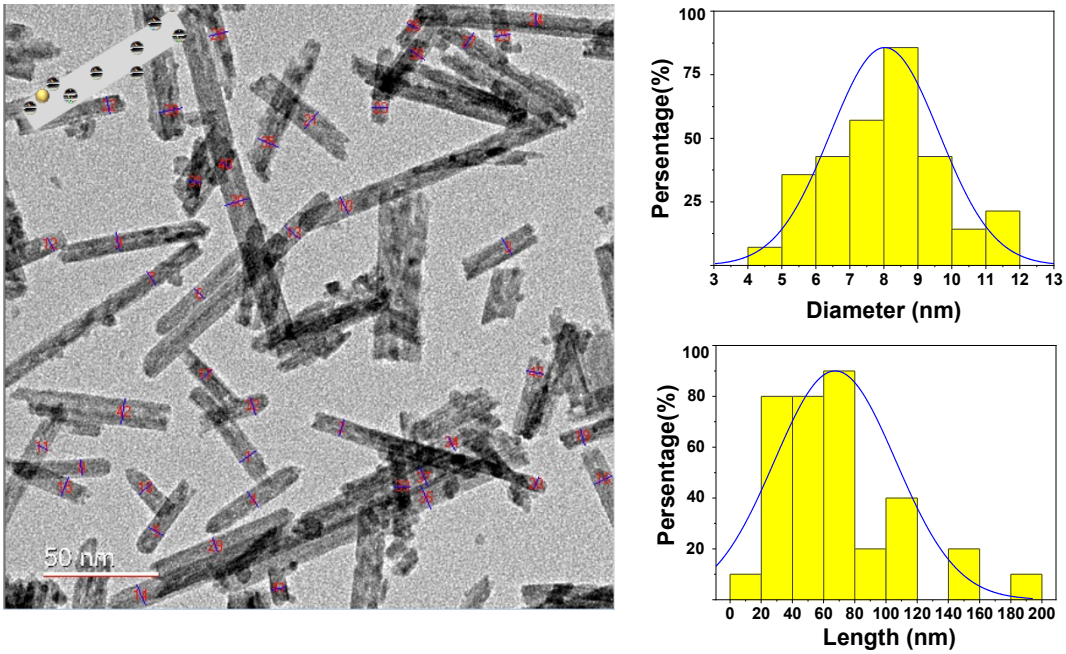

Fig. S2 TEM and particle size distribution of Pd/CeO_2 catalysts with rod morphology, with an average length of 67.4 nm and an average diameter of 8.0 nm (43 particles counted).

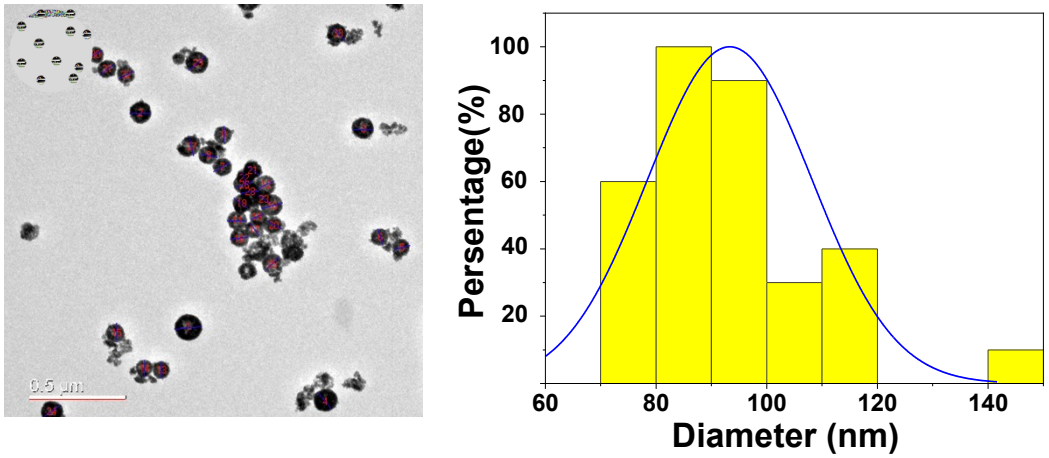

Fig. S3 TEM and particle size distribution of Pd/CeO_2 catalysts with sphere morphology, with an average diameter of 93.3 nm (33 particles counted)

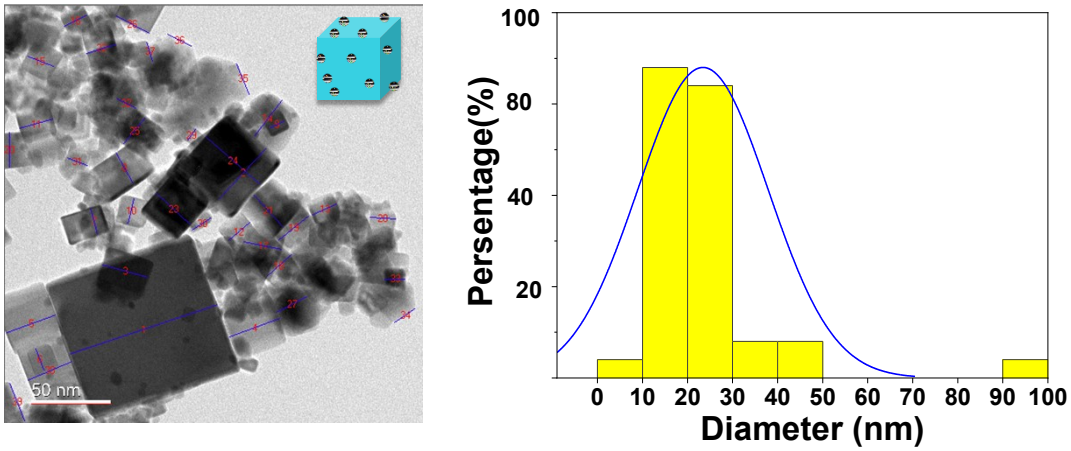

Fig. S4 TEM and particle size distribution of Pd/CeO_2 catalysts with cubic morphology, with an average diameter of 23.4 nm (39 particles counted)

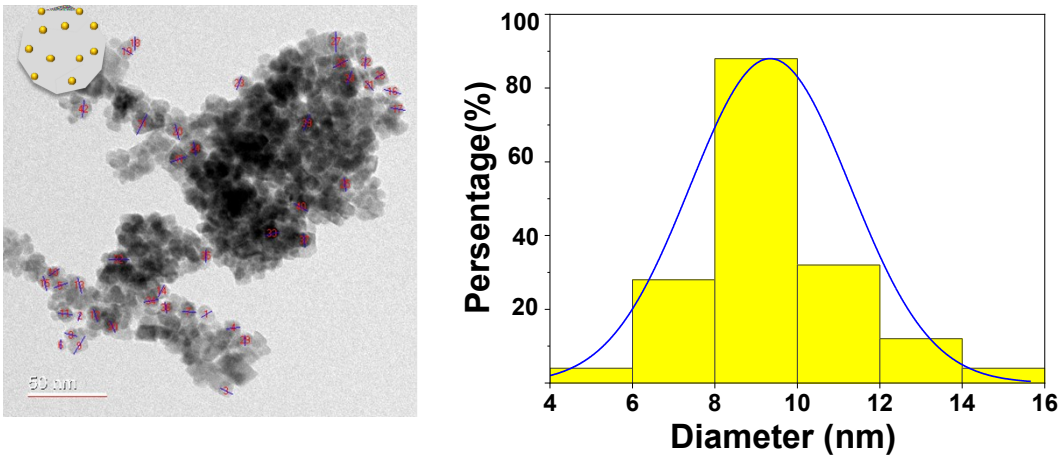

Fig. S5 TEM and particle size distribution of Pd/CeO_2 catalysts with polyhedron morphology, with an average diameter of 9.3 nm (42 particles counted).

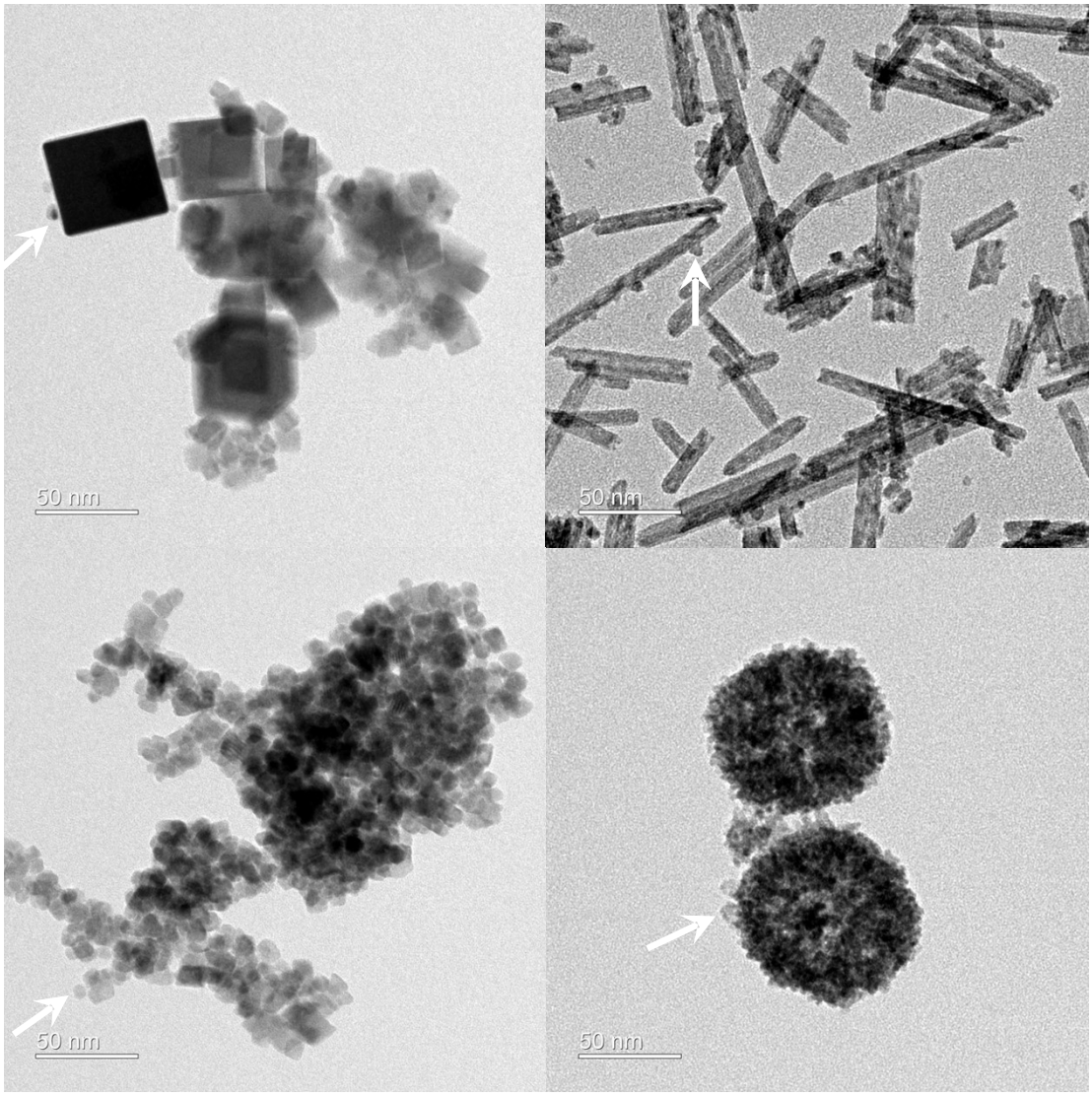

Figure S6 TEM of Pd/CeO_2 catalysts with different morphologies (palladium nanoparticles were highlighted with white arrows).

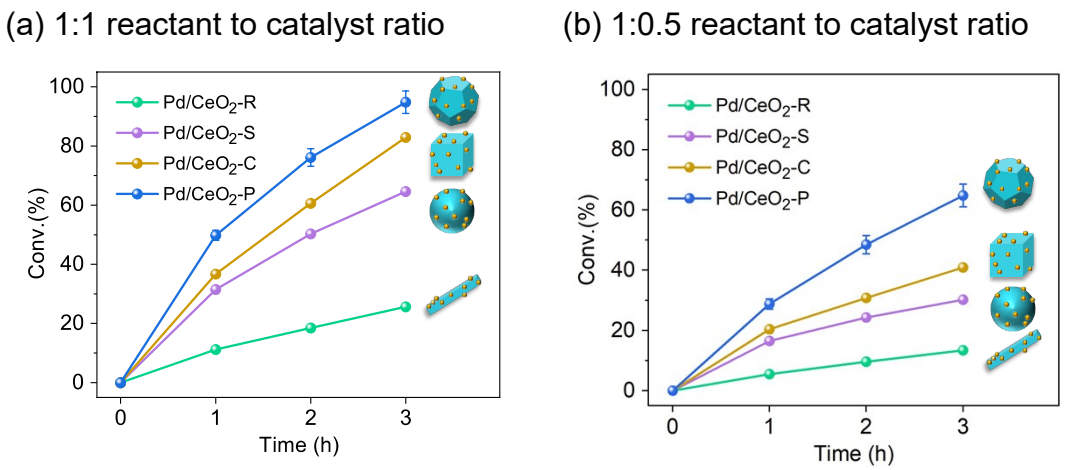

Fig.S7 *Time-dependent conversion of 2-Phenoxy-1-Phenylethanone over Pd/CeO_2 catalysts with different morphologies at a (a) 1: 1 reactant-to-catalyst ratio and (b) 1: 0.5 reactant-to-catalyst ratio.*

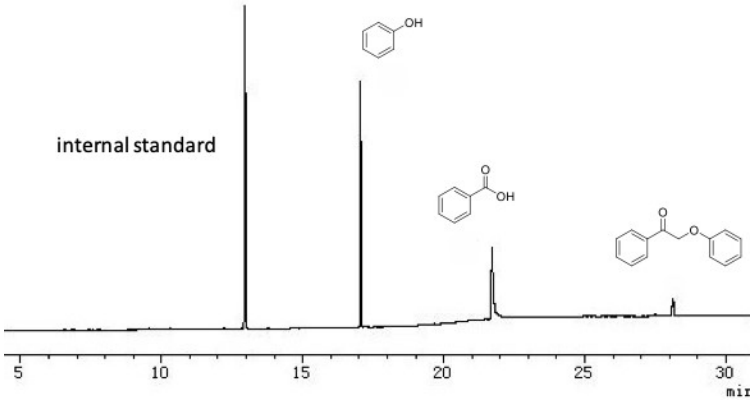

Fig. S8 Gas chromatogram of the conversion of 2-phenoxy-1-phenylethanone over the Pd/CeO_2-P catalyst at 50 °C for 3h. The internal standard (IS) is acetophenone.

Table S1 Selective Oxidative Cleavage of C-C Bonds in Lignin β-O-4 Ketones using Different Catalysts

Entry	Catalyst	Conditions	Conv.	Yields (Benzoic acid, Phenol)	Catalyst consumption (kg_{cat} per kg_{prod})	Conversion Rate(min^{-1})	Ref.
1	[PMim][NTf_2] /[$PrSO_3HMim$][OTf]	RT, 2h, UV	87.1%	78.3% 55.5%	71.77	-	[1]
2	Formic acid/F_3CSO_3H	25 °C-4 h	99.5%	96.3% 28.9%	33.94	-	[2]
3	m-CPBA/$NaHCO_3$	~ 25 °C-15 h	100%	99% -	4.25	-	[3]
4	$Cu(OAc)_2/BF_3{\cdot}OEt_2$	100 °C-3 h	99%	96% 95%	1.87	-	[4]
5	2M NaOH	50 °C-10 h	100%	88% 42%	1.36	-	[5]
6	(dipic)VV(O)(OiPr)	100 °C-48 h	~40%	19% -	1.26	-	[6]
7	CuCl	30°C-5.5 h	97%	85% 89%	0.72	-	[7]
8	HTc-Cu-V	135 °C-24 h	>95%	80% <2%	0.46	0.002	[8]
9	$Cu(NO_3)_2{\cdot}3H_2O$	120 °C-10 h	-	>99% 43%	0.31	0.015	[9]
10	CeO_2	170 °C-2 h	76%	56% 58%	1.36	-	[10]
11	15Ce-5Cu/MFI-ns	100 °C-4 h	99.9%	98.0% 85.3%	0.25 [a]	0.040	[11]
12	CTF-pDCB-1	160 °C-6 h	>99%	24.0% 45.1%	0.20 [a]	-	[12]
13	Pd/CeO_2	50 °C -3h	94.8%	85.5% 88.1%	0.13 [a]	0.346	This study

[a] Catalyst consumption was determined based on the number of cycles without deactivation reported in the literature, which means that this value can be lower.

Table S2 Catalytic conversion of 2-phenoxy-1-phenylethanone.

Entry	Catalyst	Conversion (%)	Yields (mol%)	
			benzoic acid	phenol
1	-	8.2	0.9	2.2
2	CeO_2-P	10.5	1.1	2.5
3	Pd/CeO_2-P	94.8	85.5	89.4
4 [a]	Pd + CeO_2-P	25.3	7.5	10.6

General conditions: 2-phenoxy-1-phenylethanone (0.1 mmol), catalyst (20 mg), H_2O_2(30%,0.5mL), NaOH (0.4 mmol), water solvent (2.5 mL), 50 °C, 3h. [a] Physically mixed Pd and CeO_2-P (no formal synthesis). The pure Pd powder was synthesized using the same formaldehyde reduction procedure but without the addition of any CeO_2 support.

References

[1] Y. Kang, X.M. Lu, G.J. Zhang, X.Q. Yao, J.Y. Xin, S.Q. Yang, Y.Q. Yang, J.L. Xu, M. Feng, S.J. Zhang, Metal-Free Photochemical Degradation of Lignin-Derived Aryl Ethers and Lignin by Autologous Radicals through Ionic Liquid Induction, Chemsuschem, 12 (2019) 4005-4013.

[2] X. Li, Y. Zhang, Metal Catalyst-Free Oxidative C− C Bond Cleavage of a Lignin Model Compound by H2O2 in Formic Acid, ChemSusChem, 13 (2020) 1740-1745.

[3] Y. Wang, Q. Wang, J. He, Y. Zhang, Highly effective C–C bond cleavage of lignin model compounds, Green Chemistry, 19 (2017) 3135-3141.

[4] M. Wang, L. Li, J. Lu, H. Li, X. Zhang, H. Liu, N. Luo, F. Wang, Acid promoted C–C bond oxidative cleavage of β-O-4 and β-1 lignin models to esters over a copper catalyst, Green Chemistry, 19 (2017) 702-706.

[5] A. Rahimi, A. Azarpira, H. Kim, J. Ralph, S.S. Stahl, Chemoselective metal-free aerobic alcohol oxidation in lignin, Journal of the American Chemical Society, 135 (2013) 6415-6418.

[6] B. Sedai, C. Diaz-Urrutia, R.T. Baker, R. Wu, L.P. Silks, S.K. Hanson, Comparison of copper and vanadium homogeneous catalysts for aerobic oxidation of lignin models, ACS Catalysis, 1 (2011) 794-804.

[7] Y.Z. Hu, L. Yan, X.L. Zhao, C.U. Wang, S. Li, X.H. Zhang, L.L. Ma, Q. Zhang, Mild selective oxidative cleavage of lignin C-C bonds over a copper catalyst in water, Green Chemistry, 23 (2021) 7030-7040.

[8] T. Rinesch, J. Mottweiler, M. Puche, P. Concepcion, A. Corma, C. Bolm, Mechanistic investigation of the catalyzed cleavage for the lignin β-O-4 linkage: implications for vanillin and vanillic acid formation, ACS Sustainable Chemistry Engineering, 5 (2017) 9818-9825.

[9] H.F. Liu, M. Wang, H.J. Li, N.C. Luo, S.T. Xu, F. Wang, New protocol of copper-catalyzed oxidative C(CO)-C bond cleavage of aryl and aliphatic ketones to organic acids using O-2 as the terminal oxidant, J Catal, 346 (2017) 170-179.

[10] W. Deng, H. Zhang, X. Wu, R. Li, Q. Zhang, Y. Wang, Oxidative conversion of lignin and lignin model compounds catalyzed by CeO 2-supported Pd nanoparticles, Green chemistry, 17 (2015) 5009-5018.

[11] L.X. Li, J.H. Kong, H.M. Zhang, S.J. Liu, Q. Zeng, Y.Q. Zhang, H. Ma, H.Y. He, J.X. Long, X.H. Li, Selective aerobic oxidative cleavage of lignin C-C bonds over novel hierarchical Ce-Cu/MFI nanosheets, Appl Catal B-Environ, 279 (2020).

[12] L. Zhao, S. Shi, M. Liu, G. Zhu, M. Wang, W. Du, J. Gao, J. Xu, Covalent triazine framework catalytic oxidative cleavage of lignin models and organosolv lignin, Green Chemistry, 20 (2018) 1270-1279.