Supporting Information

Size-Dependent Catalytic Performance of Ruthenium Nanoparticles in the Hydrogenolysis of β-O-4 Lignin Model Compounds

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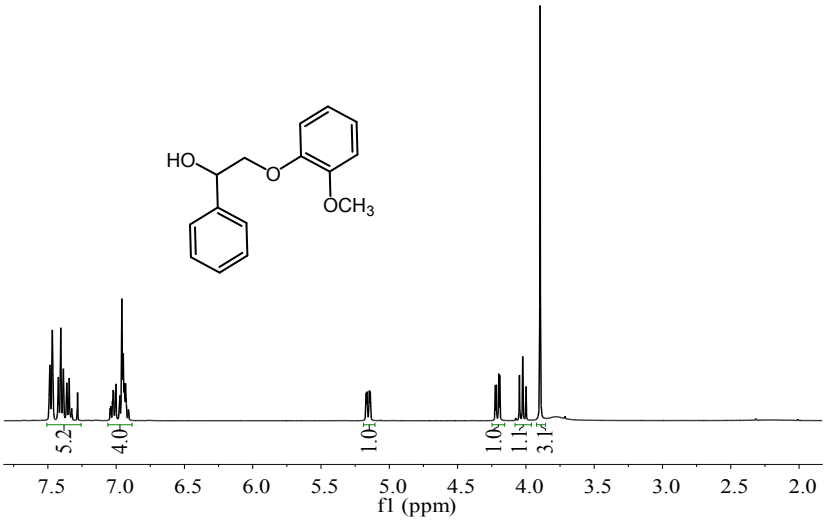


Figure S1. ^{1}H NMR spectra ($CDCl_3$) of 2-(2-methoxyphenoxy)-1-phenylethanol.

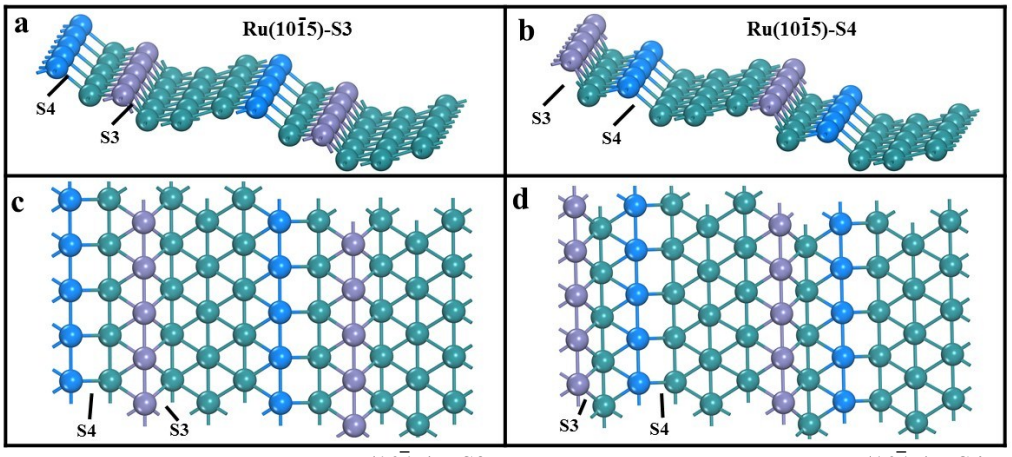


Figure S2. Calculated structures of $Ru(10\bar{1}5)$ - S3 (a, c; side and top views) and $Ru(10\bar{1}5)$ - S4 (b, d). Atoms in purple are those at steps with three-fold symmetry (S3), and those in blue at steps are with four-fold symmetry (S4).

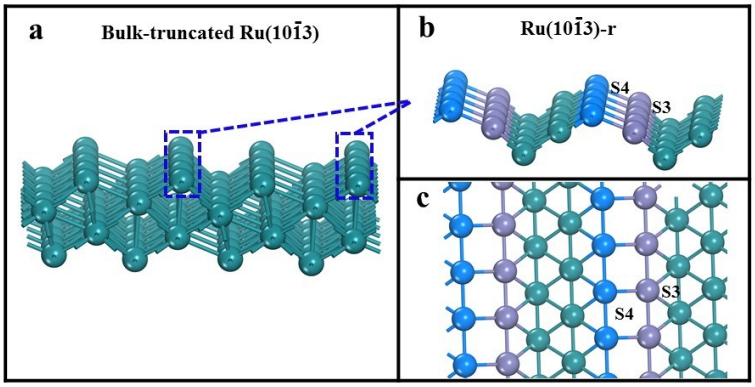
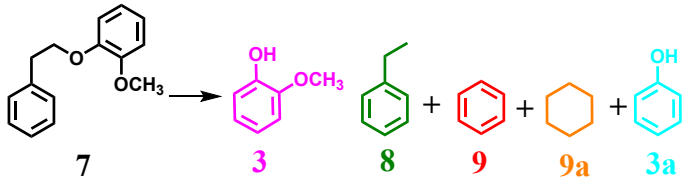


Figure S3. Calculated structures of the bulk-truncated $Ru(10\bar{1}3)$ surface (a) and $Ru(10\bar{1}3)$ - r (b, c; side and top views) with half of the dentate structural units being removed.



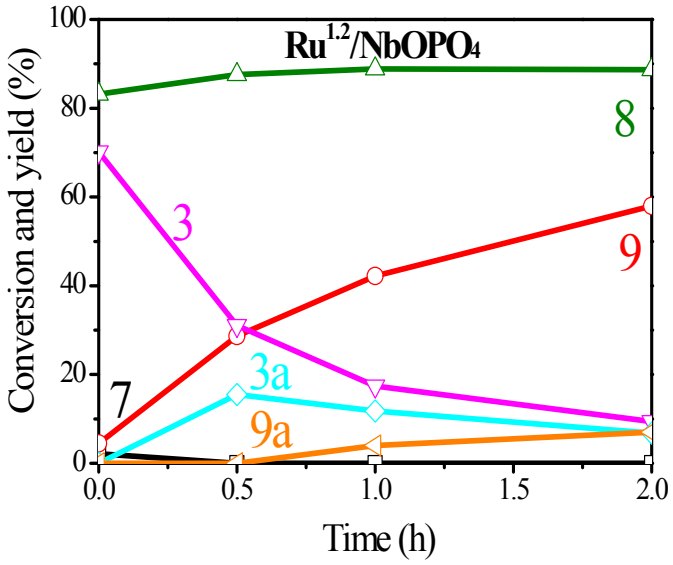


Figure S4. The product distributions versus reaction time of 1-methoxy-2-phenethoxybenzene (**7**) catalyzed by 2%$Ru^{1.2}/NbOPO_4$. Reaction conditions: substrate (0.1g), catalyst (0.05g), deionized water (14mL), 230 °C, initial H_2 pressure 0.5 MPa. The yields of products are obtained by the equation: $Y_{product} = n_{product} / n_{reactant}$, 1 mole reactant can produce 2 mole monomer products.

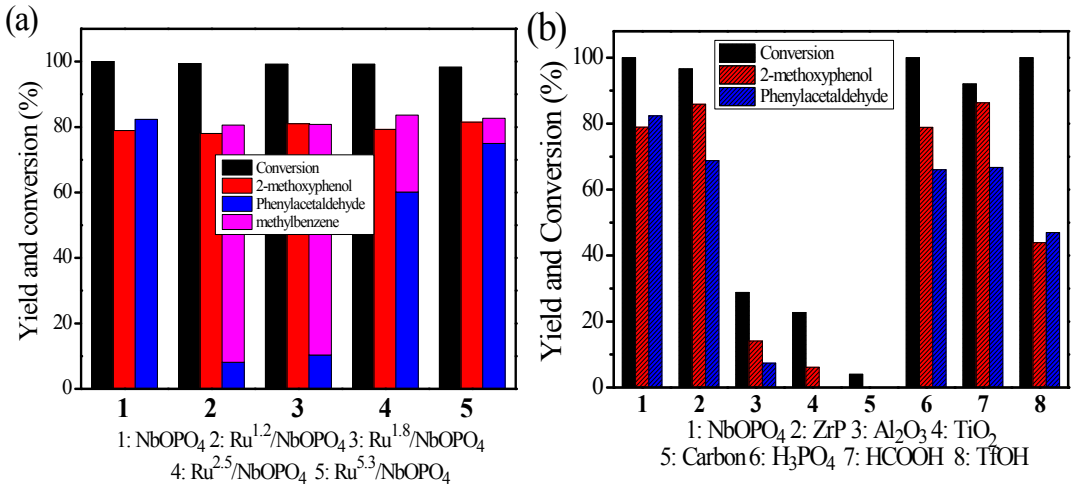
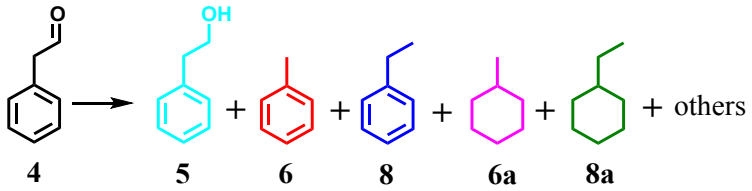


Figure S5. The acid hydrolyzation of 2-(2-methoxyphenoxy)-1-phenylethanol to aromatic hydrocarbons over diverse catalysts. (a) bare $NbOPO_4$ support and four different sized Ru/NbOPO4 catalysts. (b)$NbOPO_4$, ZrP, Al_2O_3, TiO_2, Carbon, H_3PO_4, HCOOH, and TfOH. Reaction conditions: catalyst (0.05g), substrate (0.1g), deionized water (14mL), Ar, 230°C for 4h.



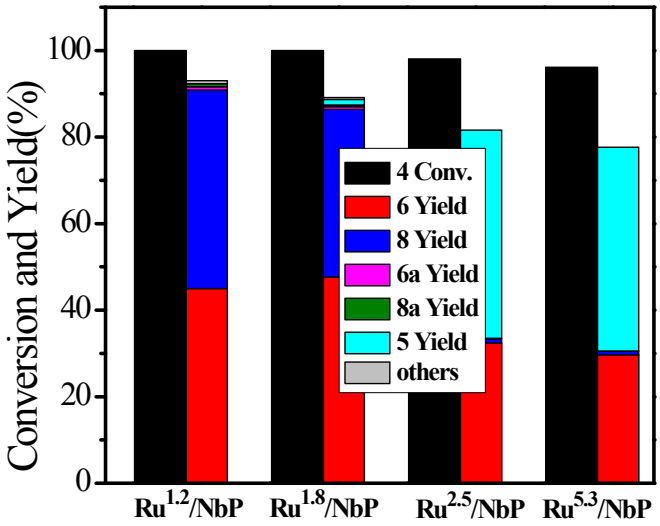


Figure S6. Reaction results for the conversion of phenylacetaldehyde over four different sized Ru/$NbOPO_4$ in a batch reactor. Reaction conditions: substrate (0.1 g), catalyst (0.05 g), deionized water (14 mL), 230 °C for 1 h, initial H_2 pressure 0.5 MPa. Others were mainly bipolymer of phenylacetaldehyde, including 1, 3-diphenylpropane and butane-1, 3-diyldibenzene.

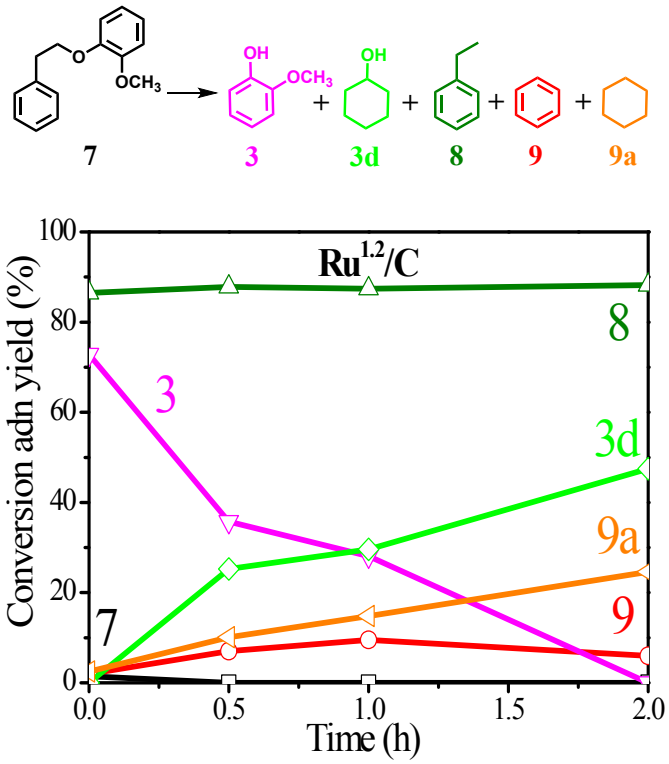


Figure S7. The product distributions versus reaction time of 1-methoxy-2-phenethoxybenzene (**7**) catalyzed by 2%$Ru^{1.2}$/C. Reaction conditions: substrate (0.1g), catalyst (0.05g), deionized water (14mL), 230 °C, initial H_2 pressure 0.5 MPa. The yields of products are obtained by the equation: $Y_{product} = n_{product} / n_{reactant}$, 1 mole reactant can produce 2 mole monomer products.

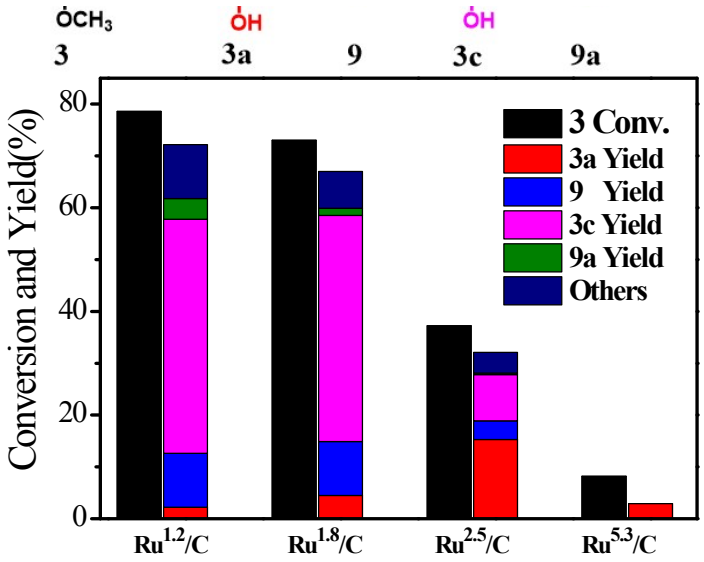


Figure S8. Reaction results for the hydrodeoxygenation of 2-methoxyphenol over different sized Ru/C in a batch reactor. Reaction conditions: substrate (0.1 g), catalyst (0.05 g), deionized water (14 mL), 230 °C for 2 h, initial H_2 pressure 0.5 MPa. Others contain anisole, 2-methoxycyclohexanol, and cyclohexanone.

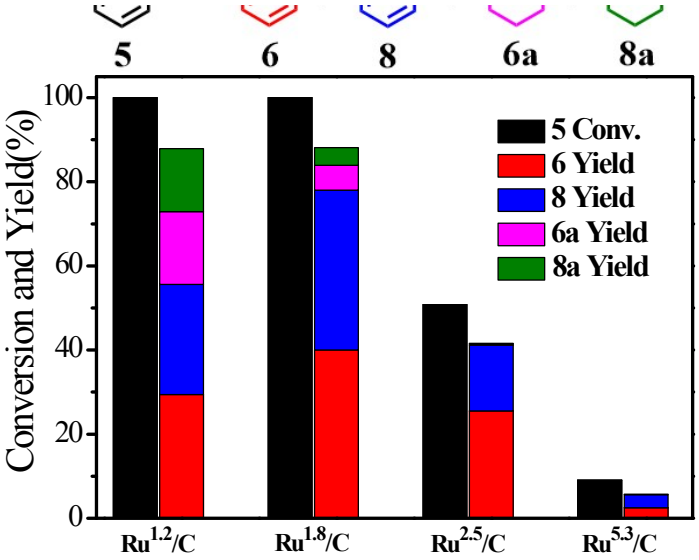
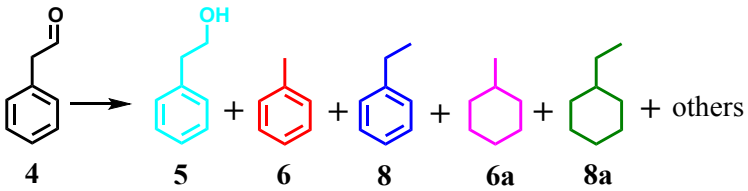


Figure S9. Reaction results for the conversion of 2-phenylethanol over different sized Ru/C in a batch reactor. Reaction conditions: substrate (0.1 g), catalyst (0.05 g), deionized water (14 mL), 230 °C for 1 h, initial H_2 pressure 0.5 MPa.



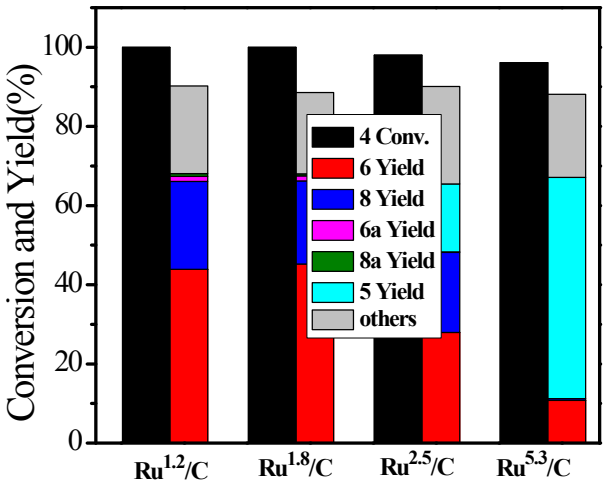
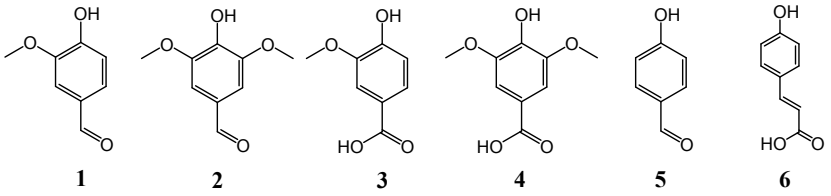


Figure S10. Reaction results for the conversion of phenylacetaldehyde over different sized Ru/C in a batch reactor. Reaction conditions: substrate (0.1 g), catalyst (0.05 g), deionized water (14 mL), 230 °C for 1 h, initial H_2 pressure 0.5 MPa. Others were mainly bipolymer of phenylacetaldehyde, including 1, 3-diphenylpropane and butane-1, 3-diyldibenzene.

Table S1. Reaction results for the alkaline nitrobenzene oxidation of lignin.[a]



Reactant	Yield (mmol/g)						Total (mmol/g)
	1	2	3	4	5	6	
birch lignin	0.51	1.98	0.05	0.2	--	--	2.74
enzymic lignin	0.41	0.45	0.09	0.14	0.26	0.09	1.45

[a]Reaction conditions: lignin (0.04g), nitrobenzene (0.4mL), 2 M NaOH (7 mL), 170°C for 2h

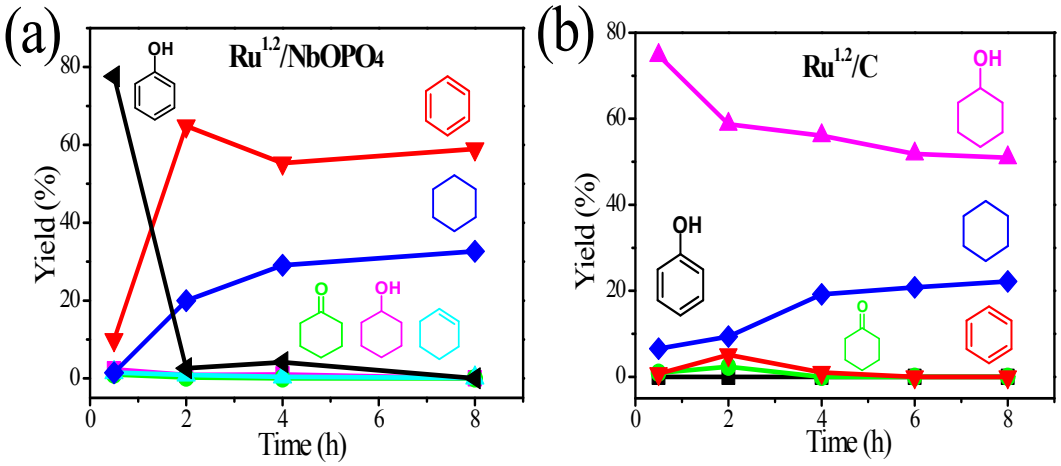


Figure S11. The time course of the phenol hydrodeoxygenation by (a) $Ru^{1.2}/NbOPO_4$, (b) $Ru^{1.2}/C$. Reaction conditions: catalyst (0.05g), substrate (0.1g), deionized water (14mL), 230oC, initial H2 pressure 0.5 MPa.

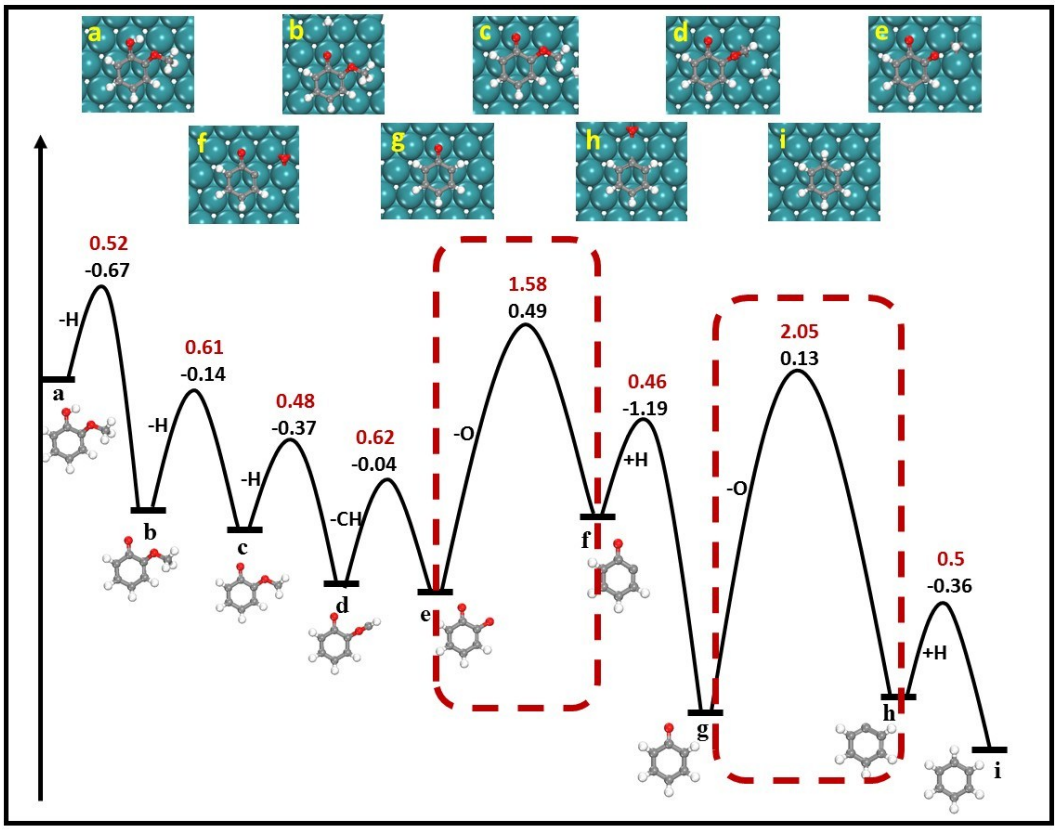


Figure S12. Calculated energy profile of the dominant reaction pathways for the hydrodeoxygenation of guaiacol to benzene over Ru(0001) surface. Numerical values over the arcs denote reaction energies (black) and activation barriers (red) of the corresponding reaction steps. The calculated structures of each intermediate in the reaction are also illustrated (a-i, top views).