## Supporting information Hydrodeoxygenation of phenol as a bio-oil model compound on intimate contact noble metal-Ni<sub>2</sub>P/SiO<sub>2</sub> catalyst

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Figure S1 demonstrates the XRD patterns of  $Ni_2P/SiO_2$  with different loadings. There is no prominent  $Ni_2P$  diffraction peak at 5% $Ni_2P/SiO_2$  compared with the other samples due to low loading and high distribution of  $Ni_2P$ . However, excess loading leads to the larger particle size of  $Ni_2P$  and correspondingly decreasing of hydrodeoxygenation activity.

Figure S2 shows phenol conversion and product selectivities at 453K and 2.0MPa for 3h on the pure noble metal. In comparison with noble metal-Ni<sub>2</sub>P/SiO<sub>2</sub>, cyclohexane and cyclohexanol products over supported noble metal catalysts decrease while cyclohexanone increases obviously.

Effect of reaction time on product selectivities over 1%Pd-10%Ni<sub>2</sub>P/SiO<sub>2</sub> was also checked in Figure S3. Results show that cyclohexane selectivity increases accompanied with the decreasing in cyclohexanol when reaction time prolongs. This means that cyclohexanol gradually converts into cyclohexane with reaction proceeding on noble metal-Ni<sub>2</sub>P/SiO<sub>2</sub>.

Catalytic evaluation of physical mixture of 0.1g of 1%Pd/SiO<sub>2</sub> and 0.1g of 10% Ni<sub>2</sub>P/SiO<sub>2</sub> has also been carried out to maintain the same active component loading, Pd and Ni<sub>2</sub>P, to 0.1g 1% Pd-10% Ni<sub>2</sub>P/SiO<sub>2</sub> for phenol hydrodeoxygenation (Table S1). However, since catalysts have doubled in total weight, this means that opportunity for reactant contacting with catalysts might be about two times higher than other reaction evaluation. Under the circumstances, catalytic performance over physical mixture of 0.1g of 1%Pd/SiO<sub>2</sub> and 0.1g of 10% Ni<sub>2</sub>P/SiO<sub>2</sub> is similar to 0.1g 1%Pd-10%Ni<sub>2</sub>P/SiO<sub>2</sub>. On one hand, activity comparison is meaningless since phenol has been converted completely over these two catalysts. On the other hand, 0.1g 1%Pd-10% Ni<sub>2</sub>P/SiO<sub>2</sub> has slight higher cyclohexane selectivity than physical mixture of 0.1g of 1%Pd/SiO<sub>2</sub> and 0.1g of 10% Ni<sub>2</sub>P/SiO<sub>2</sub>. Mixed catalyst system, however, deserves the higher cyclohexane selectivity because cyclohexanol can further convert into cyclohexane with the increasing in opportunity for reactant contacting with catalysts.

Relative surface atomic percentages with respect to Si, O and Pd on the basis of XPS analysis were also presented Table S2. Results confirm that there are more noble metal atoms on composite catalyst surface than  $SiO_2$  supported noble metal and the existence of  $Ni_2P$  facilities the formation of noble metal nanoparticle. Table S1 Comparison of catalytic performances<sup>a</sup> over  $0.1g \ 1\%Pd-10\%Ni_2P/SiO_2$  and physical mixture of 0.1g of  $1\%Pd/SiO_2$  and 0.1g of  $10\% Ni_2P/SiO_2$ .

Catalysts	Conversion (%)	Selectivity (%)				
-	Phenol	Cyclohexane	Cyclohexanone	Cyclohexanol	Benzene	
Physical mixture of 0.1g of	100	94.0	0	6.0	0	
1%Pd/SiO <sub>2</sub> and 0.1g of $10%$						
Ni <sub>2</sub> P/SiO <sub>2</sub>						
0.1g 1%Pd-10%Ni <sub>2</sub> P/SiO <sub>2</sub>	100	95.4	0	4.6	0	

<sup>a</sup> Reaction conditions: temperature 493 K, Pressure 2.0 MPa, time 3h, phenol 0.27 g, 20 mL of dodecane as a solvent

Percentage	1%Pd-10%Ni <sub>2</sub> P/SiO <sub>2</sub>	1%Pd/SiO <sub>2</sub>	1%Pt-10%Ni <sub>2</sub> P/SiO <sub>2</sub>	1%Pt/SiO <sub>2</sub>	1%Ru-10%Ni <sub>2</sub> P/SiO <sub>2</sub>	1%Ru/SiO <sub>2</sub>
Si	17.5	17.8	16.7	17.9	16.1	17.5
0	79.2	81.2	72.0	81.8	78.0	81.5
Noble metal	3.3	1.0	11.3	0.3	5.9	0.9

Table S2 Relative surface atomic percentages with respect to Si, O and Pd on the basis of XPS analysis



Figure S1



Figure S2



Figure S3