

## Selective arenes production from transfer hydrogenolysis of benzyl phenyl ether promoted by the coprecipitated Pd/Fe<sub>3</sub>O<sub>4</sub> catalyst

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**ELECTRONIC SUPPLEMENTARY INFORMATION**

## Experimental Section

2-phenethyl phenyl ether (PPE) was purchased from Frinton Laboratories and used without further purification. All other chemicals were purchased from Alfa-Aesar and used without further purification.

Pd/Fe<sub>3</sub>O<sub>4</sub> catalyst, with a nominal palladium loading of 5 wt %, was prepared by using the coprecipitation technique. An aqueous solution of palladium nitrate (Fluka) and iron(III)nitrate nonahydrate (Fluka) was added dropwise to an aqueous solution of Na<sub>2</sub>CO<sub>3</sub> (1M). The precipitate was filtered off, washed with water and dried overnight at 120 °C. Thereafter, the sample was reduced at 200 °C for 2 h under flowing hydrogen.

The benchmark catalyst Pd/C (5 wt % Pd) was purchased from commercial sources and reduced at 200 °C for 2 h under flowing hydrogen before use.

Catalytic reactions were performed in a 160 mL stainless-steel reactor (Parr Instruments). The reactor was loaded with a suspension of the catalyst (0.25 g) in a solution of the desired substrate in 2-propanol (60 mL, 0.1 M). The reactor was purged with N<sub>2</sub> (99.99%), the system was then pressurized with the desired gas (N<sub>2</sub> or H<sub>2</sub>), stirred at 500 rpm, and, finally, heated up to the reaction temperature. The reaction time started after reaching the desired temperature. The heating rate was well reproduced in the experiments. At the end of the reaction, the reactor was cooled to RT, the pressure released and the composition of the organic phase was analyzed by gas chromatography.

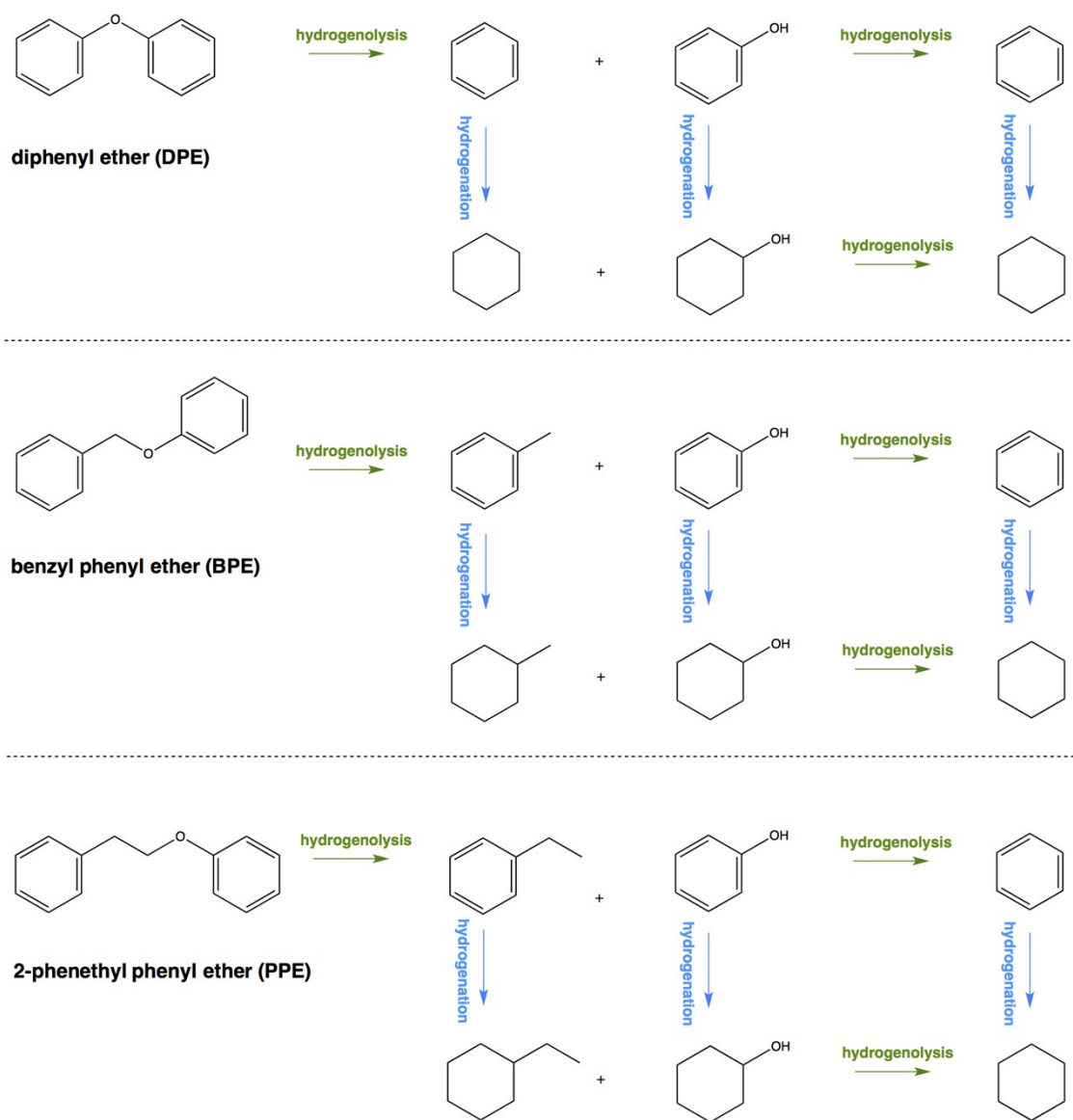
For any recycling test, after each run, the catalyst was filtered, washed thoroughly with 2-propanol and reused with fresh reactants under the same reaction conditions.

Gas chromatographic analyses were performed on a HP 5890 gas chromatograph equipped with a wide-bore capillary column (CP- WAX 52CB, 60 m, i.d. 0.53 mm) and flame ionization detector. Conversion and selectivity to the product (i) were calculated on the basis of Equations (1) and (2), respectively.

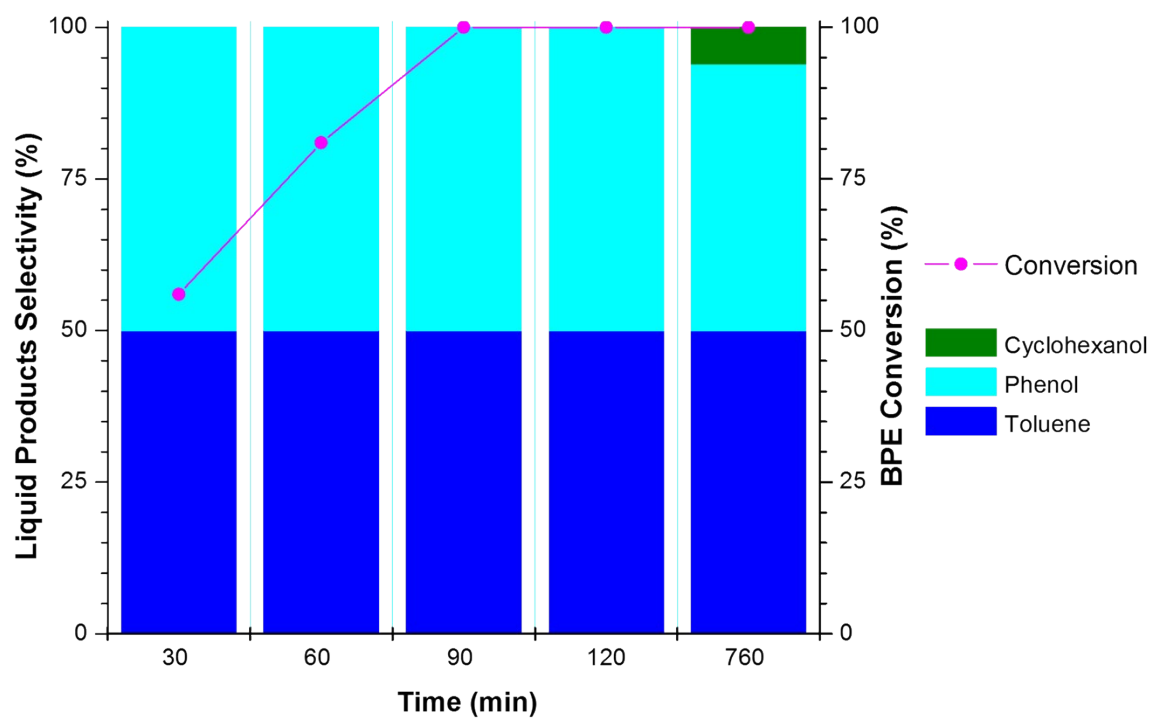
$$\text{Conversion} = \frac{n_i(\text{sub}) - n_t(\text{sub})}{n_i(\text{sub})} \times 100 [\%] \quad \text{Eq.1}$$

$$\text{Selectivity} = \frac{n_t(i)}{n_t(\text{sub})} \times 100 [\%] \quad \text{Eq.2}$$

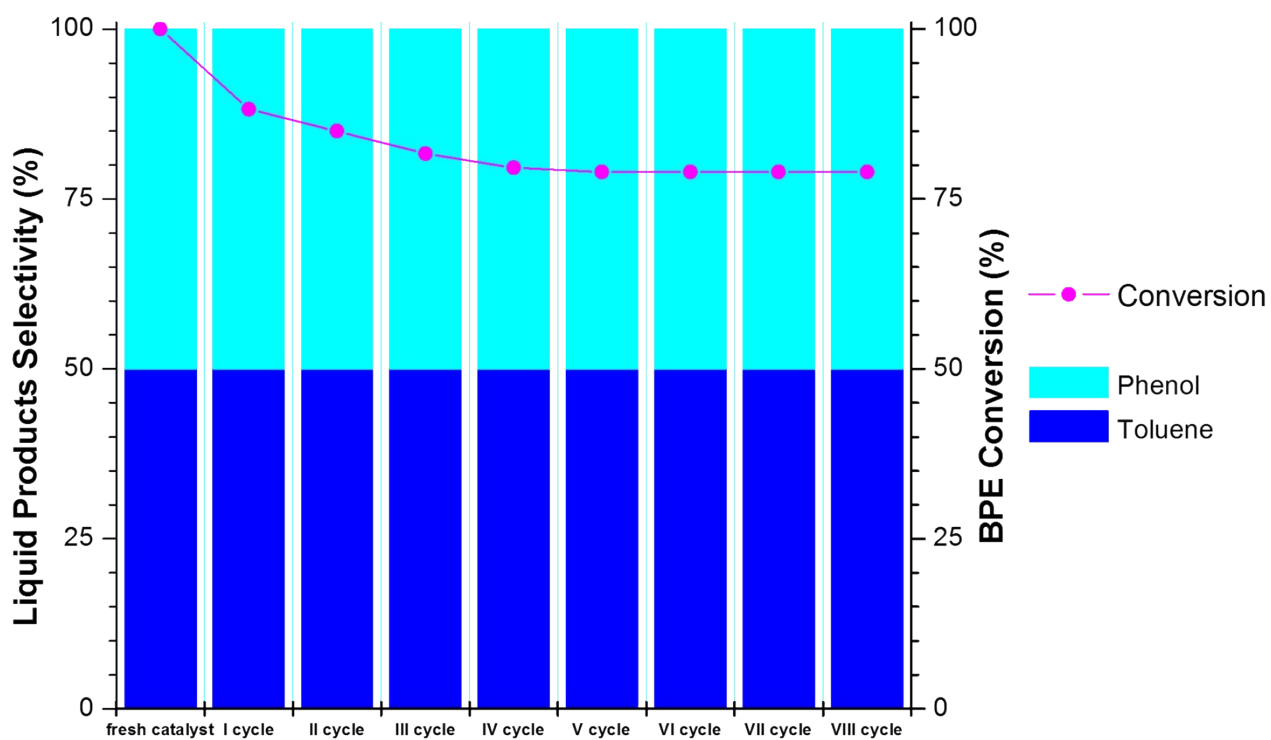
$n_i$  :molar amount of the defined substrate at time 0;  $n_t$  :molar amount of the defined substrate at time t;  $n_t(i)$  :molar amount of the product (i) at time t.



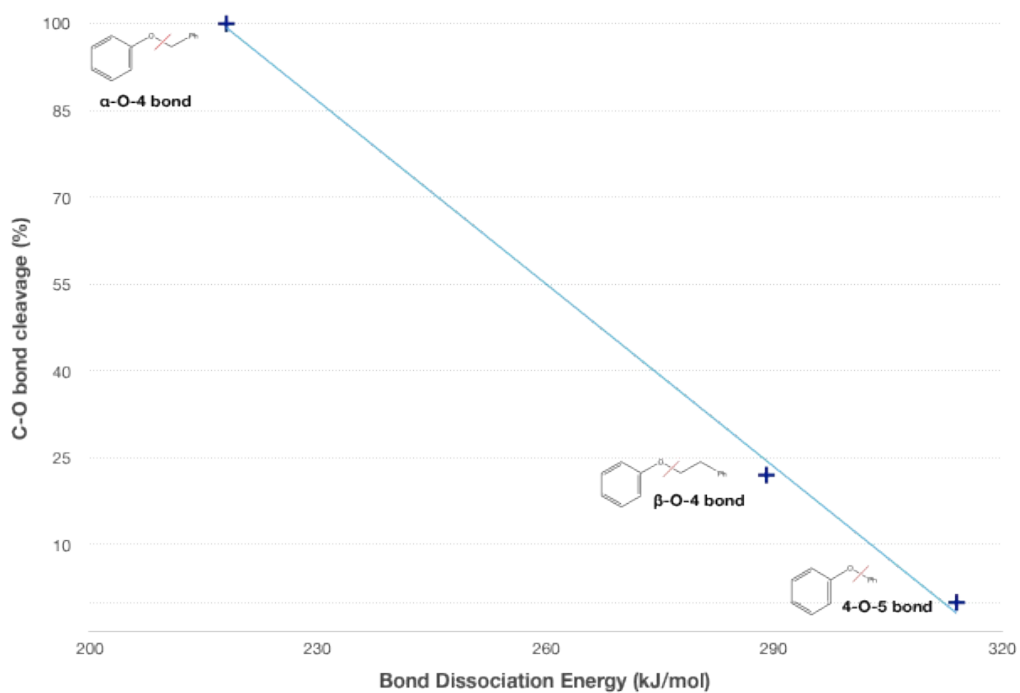
**Scheme S1.** Major reaction pathways (hydrogenolysis and hydrogenation processes) for conversion of benzyl phenyl ether (BPE), 2-phenethyl phenyl ether (PPE) and diphenyl ether (DPE).



**Figure S1.** Reaction time effect on the BPE conversion (%) and liquid products selectivity (%) in the CTH at 240 °C.



**Figure S2** Re-use of the Pd/Fe<sub>3</sub>O<sub>4</sub> catalyst in the transfer hydrogenolysis of BPE (240°C; 90 min; 0,25 g catalyst; 60ml entry solution 0.1 M; 10 bar N<sub>2</sub> pressure).



**Figure S3.** C–O cleavage (%) vs bond dissociation energy (kJ/mol) in the CTH of model substrates of  $\alpha$ -O-4,  $\beta$ -O-4 and 4-O-5 lignin linkages.

<b>Catalyst</b>	<b>Temp [°C]</b>	<b>Time [hours]</b>	<b>BPE Conversion [%]</b>	<b>Aromatic Selectivity [%]</b>
Pd/Fe <sub>3</sub> O <sub>4</sub>	210	12	100	99,0
Pd/Fe <sub>3</sub> O <sub>4</sub>	210	6	100	100
Pd/Fe <sub>3</sub> O <sub>4</sub>	210	3	81,4	100
Pd/Fe <sub>3</sub> O <sub>4</sub>	180	12	41,0	100
Pd/Fe <sub>3</sub> O <sub>4</sub>	180	6	40,0	100
Pd/Fe <sub>3</sub> O <sub>4</sub>	180	3	30,2	100

**Table S1.** Reaction time effect on the BPE conversion (%) and aromatic selectivity (%) in the CTH at 180 and 210°C promoted by Pd/Fe<sub>3</sub>O<sub>4</sub> catalyst (0,25 g catalyst; 60 ml entry solution 0.1 M; 10 bar N<sub>2</sub>).

<b>Catalyst</b>	<b>H<sub>2</sub> pressure [bar]</b>	<b>BPE Conversion [%]</b>	<b>Aromatic Selectivity [%]</b>
Pd/Fe <sub>3</sub> O <sub>4</sub>	10	75	100
Pd/Fe <sub>3</sub> O <sub>4</sub>	20	73	100
Pd/Fe <sub>3</sub> O <sub>4</sub>	40	71	98

**Table S2.** Hydrogenolysis of BPE promoted by the Pd/Fe<sub>3</sub>O<sub>4</sub> catalyst (0,25 g catalyst; 90 min, 60 ml entry solution 0.1 M).



Catalyst	Temp [°C]	BPE Conversion [mol/l]	Solvent dehydrogenation [mol/l]	Aromatic Selectivity [%]
Pd/C	180	-	-	-
Pd/C	210	0,004	0,005	100
Pd/C	240	0,008	0,011	100

**Table S3.** Catalytic Transfer Hydrogenolysis of BPE promoted by the Pd/C catalyst (0,25 g catalyst; 90 min, 60 ml entry solution 0.1 M, 10 bar N<sub>2</sub>).