Supporting Information

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Controlling Reaction Routes in Noble-Metal-Catalyzed Conversion of Aryl Ethers

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1. Experimental Section

Chemicals and catalysts

The chemicals were purchased from commercial suppliers and used as provided: diphenyl ether (Sigma-Aldrich, >99% gas chromatography (GC) assay), cyclohexyl phenyl ether (Sigma-Aldrich, >95% GC assay), benzene (Sigma-Aldrich, >99.5% GC assay), phenol (Sigma-Aldrich, >99% GC assay), cyclohexanone (Sigma-Aldrich, >99% GC assay), cyclohexanol (Sigma-Aldrich, >99% GC assay), dichloromethane (Sigma-Aldrich, >99.5% GC assay), decahydronaphthalene, mixture of cis + trans (Sigma-Aldrich, anhydrous, ≥99%), 5 wt.% Ru/C (Sigma-Aldrich), 5 wt.% Rh/C (Sigma-Aldrich), 5 wt.% Pd/C (Sigma-Aldrich), H2 (>99.999%), N2 (> 99.999%), deuterium [D2] (Sigma-Aldrich, 99.9 atom% D), and normal H2O (Milli-Q, ultrapure water dispenser system). The lower metal loading catalysts—0.25 wt.% Ru/C and 0.25 wt.% Rh/C—were obtained by physically mixing original catalysts with activated carbon.

Transmission electron micrographs (TEM) were acquired on a JEM-2010 Jeol transmission microscope operated at 120 kV. Before TEM measurements, the samples were dispersed in methanol on a carbon-coated Cu grid. For H2 chemisorption measurements, the catalysts were pretreated under 0.1 MPa H2 at 473 K for 4 h and then held under vacuum at 473 K for 1 h. The H2 adsorption isotherms (chemisorption and physisorption) were recorded at 0.7 to 60 kPa at 308 K. Following the first isotherms, the samples were outgassed for 1 h to remove the physisorbed H2, and then another adsorption isotherm (physisorption) was recorded. The metal dispersions were obtained from the difference between extrapolated intercepts of the first and second isotherms, assuming an H:metal atomic ratio of 1.

Metal catalysts (i.e., 0.5 wt.% Ru, 0.5 wt.% Rh, and 1.0 wt.% Pd) were prepared supported on activated carbon according to the electrostatic adsorption procedure reported by Regalbuto et al. [1,2] The 5 wt.% Ir supported on activated carbon catalyst was synthesized using the incipient wetness impregnation method. Catalysts were calcined under He at 200°C for 4 hours, and then reduced at 200°C, 300°C, 350°C, or 450°C under H2. Metal loading was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES). Turnover rates of the reactions on self-made catalysts were calculated on the number of total metal atoms.

Catalyst tests

The reactions were carried out in Parr autoclaves (Series 4848, 300 mL reactor for aqueous phase reactions and 100 mL reactor for decalin) in the presence of H2. First, the catalyst and solvent were loaded into the reactor at room temperature. After the reactor was flushed with H2 three times, the autoclave was pressurized with H2 to 40 bar, and the reaction was conducted at the desired temperature at a stirring speed of 700 rpm. The H2 pressure was corrected by considering the non-ideal gas behavior, the solubility of H2 in the solvent and the temperature dependence of solvent density. [3–6] After the reaction, the reactor was quenched to ambient temperature in an ice/water mixture, and the contents in the reactor from aqueous phase were extracted using dichloromethane and analyzed using an Agilent 7890A GC equipped with a HP-5MS 25 m x 0.25 µm (inner diameter) column, coupled with Agilent 5975C mass spectrometer. Products from reactions in decalin were measured directly after the dilution by dichloromethane. 1,3-Dimethoxybenzene was used as an internal standard for quantification purposes. The carbon balances for all the reported experiments were 90 ±5%. The turnover frequency (TOF) was calculated from conversion <20 % and based on the number of surface metal atoms measured by H2 chemisorption. Because benzene and cyclohexane are generated only by hydrogenolysis (no cleavage of aromatic and aliphatic C–OH), the C-based selectivity of hydrogenolysis is twice the summed selectivity of benzene and cyclohexane. The selectivity to hydrolysis is calculated by subtracting the selectivities to hydrogenolysis and hydrogenation from 100%.
2. Additional information

The reductive conversion of diphenyl ether (Ph$_2$O) was evaluated from low to higher conversion in decalin and water over three commercially available 5 wt.% carbon supported (Ru, Rh, and Pd) catalysts. The average particle sizes (3–6 nm) and dispersion (23 %–31 %) of the metals were characterized by TEM and H$_2$ chemisorption measurements (Figure S6 and Table S12). Ph$_2$O was fully converted after 6 hours in water or decalin with low dosage of the catalysts (substrate:metal $\approx$ 8000:1) (Table S13). The selectivity to hydrogenolysis on the metals scale as Ir (25%) $>$ Ru (20%) $\approx$ Pt (19%) $>$ Rh (10%) $>$ Pd (2%) in decalin and water (Table S13). For hydrolysis, Pd showed the highest selectivity (84%) at full conversion and Ru and Rh were similar (42%) while Pt showed the lowest selectivity (18%) (Table S13). The overall selectivities of different reaction pathways changed during the reaction (Figures S4–S9) because the primary product from hydrogenation of Ph$_2$O, cyclohexyl phenol ether was further hydrogenated or cleaved. Thus, to focus on the primary reactions, conversions of Ph$_2$O were maintained below 20% by varying the reaction time and catalyst loading for different catalysts in water and decalin.
3. Derivation of the rate equations and fitting

We derive the kinetic expressions for the proposed mechanisms of hydrogenolysis in the main text based on the conventional Langmuir–Hinshelwood model with the following assumptions:

(i) \( \text{H}_2 \) adsorbs dissociatively on the metal surface.

(ii) The coverage of reaction intermediates and products are negligible at low conversions, so the most abundant compounds on the active sites are the reactants.

1) Within the mechanistic framework proposed in Scheme 1 (main text), we first assume adsorption for reactants are quasi-equilibrated:

\[
\text{H}_2 \text{ adsorption: } \text{H}_2(\text{g}) + 2^* \rightleftharpoons 2^* \quad (K_{\text{ads,H}_2})
\]

\[
\text{Ether adsorption: } \text{R-O-C}_6\text{H}_5(\text{i}) + ^* \rightleftharpoons \text{R-O-C}_6\text{H}_5^* 
\quad (K_{\text{ads, R-O-C}_6\text{H}_5})
\]

Assuming any of the above steps to be rate-determining does not lead to rate expressions consistent with the observed reaction orders.

2) Applying site balance to all surface species, we have:

\[ [^*]_0 = [^*] + [^*\text{H}] + [\text{R-O-C}_6\text{H}_5^*] + \Sigma[\text{Intermediates}^*] \]

where \([^*]_0\) is the total number of exposed metal sites, and \(\Sigma[\text{Intermediates}^*]\) is the sum of the coverage of reaction intermediates and products. For ether adsorption on \(^*_n\), because reaction orders in ether concentration are consistently zero order, we assume that the fraction of sites covered by adsorbed ether is at its maximum (i.e., \([\text{R-O-C}_6\text{H}_5^*] = [E]_{\text{max}}\) does not change by varying the ether concentration. Therefore, we define the remainder of the sites, \([^*]_0 = [^*]_0 - [\text{R-O-C}_6\text{H}_5^*] - \Sigma[\text{Intermediates}^*] \approx [^*]_0 - [E]_{\text{max}}\). We assume the hydrogen does not compete for the same sites with the ether. Then \([^*]_0 = [^*]_0/(1 + (K_{\text{ads,H}_2}[\text{H}_2])^{0.5}) \) and \([\text{H}^*] = [^*]_0(K_{\text{ads,H}_2}[\text{H}_2])^{0.5}/(1 + (K_{\text{ads,H}_2}[\text{H}_2])^{0.5}) \).

3a) Hydrogenolysis on Rh, Pd and Pt (reaction order in \(\text{H}_2\) is 0.5)

The first hydrogen addition is quasi-equilibrated:

\[
\text{R-O-C}_6\text{H}_5^* + \text{H}^* \rightleftharpoons \text{R-O-C}_6\text{H}_6^* +^* 
\quad K_{\text{H}_1} = (k_1/k_{-1})
\]

where \(k_1\) and \(k_{-1}\) are the forward and reverse rate constants for the first \(\text{H}\) addition step.

The C-O bond cleavage is rate determining:

\[
\text{R-O-C}_6\text{H}_6^* + ^* \rightarrow \text{C}_6\text{H}_6^* + \text{R-O}^* 
\]

\[
r_{\text{rds}} = k_{\text{rds}}K_{\text{H}_1}[E_{\text{max}}][^*]_0^{0.5}(K_{\text{H}_2,\text{ads}[\text{H}_2])^{0.5}/(1 + (K_{\text{H}_2,\text{ads}[\text{H}_2])^{0.5})}
\]

3b) Hydrogenolysis on Ru and Ir (reaction order in \(\text{H}_2\) is 1)

The first and second hydrogen additions are quasi-equilibrated:

\[
\text{R-O-C}_6\text{H}_5^* + \text{H}^* \rightleftharpoons \text{R-O-C}_6\text{H}_6^* +^* 
\quad K_{\text{H}_1} = (k_1/k_{-1})
\]

\[
\text{R-O-C}_6\text{H}_6^* + \text{H}^* \rightleftharpoons \text{R-O-C}_6\text{H}_7^* +^* 
\quad K_{\text{H}_2} = (k_2/k_{-2})
\]

where \(k_1\) and \(k_{-1}\) are the forward and reverse rate constants for the first or second \(\text{H}\) addition step.
The C–O bond cleavage is rate determining:

\[ \text{R-O-C}_6\text{H}_7\text{^*}_n + * \rightarrow \text{C}_6\text{H}_7\text{^*}_n + \text{R-O^*} \]

\[ r_{\text{rds}} = k_{\text{rds}}K_1\text{H}K_2\text{H}[^E_{\text{max}}][^*]_0 \frac{K_{\text{H}_2\text{ads}}[\text{H}_2]}{1 + (K_{\text{H}_2\text{ads}}[\text{H}_2])^{0.5}} \]

4a) Hydrogenation on Rh, Pd, Ir, and Pt (reaction order in H\(_2\) is 1)

The first hydrogen addition is quasi-equilibrated:

\[ \text{R-O-C}_6\text{H}_5\text{^*}_n + \text{H^*} \rightleftharpoons \text{R-O-C}_6\text{H}_6\text{^*}_n + * \quad K_{\text{1H}} = \left( \frac{k_1}{k_{-1}} \right) \]

(see 3 a).

The second hydrogen addition is rate determining:

\[ \text{R-O-C}_6\text{H}_6\text{^*}_n + \text{H^*} \rightarrow \text{C}_6\text{H}_7\text{^*}_n + * \]

\[ r_{\text{rds}} = k_{\text{rds}}K_1\text{H}[^E_{\text{max}}][^*]_0 \frac{K_{\text{H}_2\text{ads}}[\text{H}_2]}{1 + (K_{\text{H}_2\text{ads}}[\text{H}_2])^{0.5}} \]

4b) Hydrogenation on Ru (reaction order in H\(_2\) is 1.5)

The first and second hydrogen additions are quasi-equilibrated:

\[ \text{R-O-C}_6\text{H}_5\text{^*}_n + \text{H^*} \rightleftharpoons \text{R-O-C}_6\text{H}_6\text{^*}_n + * \quad K_{\text{1H}} = \left( \frac{k_1}{k_{-1}} \right) \]

\[ \text{R-O-C}_6\text{H}_6\text{^*}_n + \text{H^*} \rightleftharpoons \text{R-O-C}_6\text{H}_7\text{^*}_n + * \quad K_{\text{2H}} = \left( \frac{k_2}{k_{-2}} \right) \]

(see 3 b)

The third hydrogen addition is rate determining:

\[ \text{R-O-C}_6\text{H}_7\text{^*}_n + \text{H^*} \rightarrow \text{C}_6\text{H}_8\text{^*}_n + * \]

\[ r_{\text{rds}} = k_{\text{rds}}K_1\text{H}K_2\text{H}[^E_{\text{max}}][^*]_0 \frac{(K_{\text{H}_2\text{ads}}[\text{H}_2])^{1.5}}{1 + (K_{\text{H}_2\text{ads}}[\text{H}_2])^{0.5}} \]
**Figure S1:** Experimental dependence of the reaction rates on the H₂ pressure in decalin at 150°C and fits (solid lines) with the rate equations derived in Section 3 using H₂ adsorption equilibrium constants $K_{H2,ads}$ at reaction temperatures (Table S1) for A) Hydrogenolysis and B) Hydrogenation.

**Figure S2:** Chemisorption isotherms at 35°C and fits obtained using the Langmuir model for dissociative adsorption of diatomic gases.
We used the Langmuir equation for dissociative adsorption to fit the experimental chemisorption data to obtain equilibrium adsorption constants $K_{\text{H}_2,\text{ads}}$ at 35°C for H$_2$:

\[
V = V_\infty \frac{(K_{\text{ads},\text{H}_2}[\text{H}_2])^{0.5}}{(1 + K_{\text{ads},\text{H}_2}[\text{H}_2])^{0.5}}
\]

$V$ corresponds to the volume adsorbed and $V_\infty$ to the volume absorbed at full coverage of the metal surface. $[\text{H}_2]$ is the partial pressure of H$_2$.

We used an adapted version of the van’t Hoff equation to calculate H$_2$ equilibrium adsorption constants $K_{\text{H}_2,\text{ads}}$ at reaction temperature (150°C):

\[
\ln \frac{K_{\text{ads, H}_2,T_2}}{K_{\text{ads, H}_2,T_1}} = \frac{\Delta_r H^\theta}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)
\]

$\Delta_r H^\theta$ is the standard reaction enthalpy (in this case the heat of H$_2$ adsorption) and $R$ is the ideal gas constant. $T_2$ and $T_1$ are 150°C and 35°C, respectively.

**Table S1: H$_2$ adsorption equilibrium constants $K_{\text{H}_2,\text{ads}}$ at 35 and 150°C.**

| Metal | $E_{\text{ads}}$ (H$_2$) / kJ/mol | $K_{\text{H}_2,\text{ads}}$ at 35°C | $K_{\text{H}_2,\text{ads}}$ at 150°C |
|-------|---------------------------------|---------------------------------|---------------------------------|
| Ru    | 71                              | 0.0054                          | 2.9·10$^{-6}$                   |
| Rh    | 100                             | 0.60                            | 1.5·10$^{-5}$                   |
| Pd    | 97                              | 0.74                            | 2.5·10$^{-5}$                   |
| Ir    | 96                              | 0.32                            | 1.2·10$^{-5}$                   |
| Pt    | 67                              | 0.004                           | 3.3·10$^{-6}$                   |

Heat of adsorptions for the calculations were chosen from literature (Table 1). Based on our observation that the reaction orders in H$_2$ stayed constant over a vast range of H$_2$ pressures (4–40 bar), we assume that the coverage of the metals with H$_2$ is relatively low. According to that observation, we selected the heats of adsorption of H$_2$ at low coverages.
4. Supplementary figures and tables

Figure S3. Reaction orders in H₂ pressure for hydrogenation (A), hydrogenolysis (B), and hydrolysis (C) of diphenyl ether on metal catalysts in water. Reaction conditions: 5 wt.% (10.0 mg or 1.0 mg) metal/C, 10 mmol ether, 40 mL decalin, 150°C, stirring at 700 rpm. H₂ pressure varies from 20 to 60 bar at room temperature. TOFs were calculated at <20 % conversion.
Figure S4. Illustration of changes in selectivity on Pt, Ir, Rh and Pd in water following different strategies, Step 1: reaction temperature increased from 100 to 200°C at 40 bar H₂ pressure. Step 2: KOH is added from 0 mM to 10 mM at 200°C and 65 bar H₂. Step 3: H₂ pressure decreased from 65 bar to 10 bar at 200°C in 10 mM KOH solution.
Figure S5. Comparison of the selectivity of different reaction pathways of diphenyl ether on commercial and self-made Ru, Rh, and Pd catalysts. Self-made catalysts were pre-reduced under 200°C, 300°C, and 450°C. Reaction conditions: 10 mmol ether, 80 mL water, 10 mg 5 wt.% metal/C or 50 mg ~1 wt.% metal/C, 40 bar of H₂ at room temperature, 200°C. Selectivities were calculated at <20 % conversion. Details are shown in Table S11.

Figure S6. TEM images of the metal catalysts. (A) Ru, (B) Pt, (C) Rh, (D) Pd and (E) Ir. (more than 500 particles were counted for the analysis).
Figure S7. Time-yield plots (A), conversion-yield plots (B), and distributions of the reaction pathways plots (C) for the reaction of diphenyl ether on Ru catalyst in decalin. In (B), C₆ represents benzene, cyclohexene, and cyclohexane; C₆-OH represents phenol, cyclohexanone, and cyclohexanol. Reaction conditions: 10 mmol ether, 40 mL decalin, 10 mg 5 wt.% Ru/C, 40 bar of H₂ at room temperature, 150°C.
Figure S8. Time-yield plots (A), conversion-yield plots (B) and distributions of the reaction pathways plots (C) for the reaction of diphenyl ether on Rh catalyst in decalin. In (B), C₆ represents benzene, cyclohexene, and cyclohexane; C₆-OH represents phenol, cyclohexanone and cyclohexanol. Reaction conditions: 10 mmol ether, 40 mL decalin, 20 mg 0.25 wt.% Rh/C, 40 bar of H₂ at room temperature, 150°C.
Figure S9. Time-yield plots (A), conversion-yield plots (B) and distributions of the reaction pathways plots (C) for the reaction of diphenyl ether on Pd catalyst in decalin. In (B), C₆ represents benzene, cyclohexene, and cyclohexane; C₆-OH represents phenol, cyclohexanone, and cyclohexanol. Reaction conditions: 10 mmol ether, 40 mL decalin, 10 mg 5 wt.% Pd/C, 40 bar of H₂ at room temperature, 150°C.
Figure S10. Time-yield plots (A), conversion-yield plots (B), and distributions of the reaction pathways plots (C) for the reaction of diphenyl ether on Pt catalyst in decalin. In (B), C₆ represents benzene, cyclohexene, and cyclohexane; C₆-OH represents phenol, cyclohexanone and cyclohexanol. Reaction conditions: 10 mmol ether, 40 mL decalin, 10 mg 5 wt.% Pt/C, 40 bar of H₂ at room temperature, 150°C.
Figure S11. Time-yield plots (A), conversion-yield plots (B) and distributions of the reaction pathways plots (C) for the reaction of diphenyl ether on Ir catalyst in decalin. In (B), C₆ represents benzene, cyclohexene, and cyclohexane; C₆-OH represents phenol, cyclohexanone, and cyclohexanol. Reaction conditions: 10 mmol ether, 40 mL decalin, 10 mg 5 wt.% Ir/C, 40 bar of H₂ at room temperature, 150°C.
Figure S12. Time-yield plots (A), conversion-yield plots (B) and distributions of the reaction pathways plots (C) for the reaction of diphenyl ether on Ru catalyst in water. In (B), C₆ represents benzene, cyclohexene, and cyclohexane; C₆-OH represents phenol, cyclohexanone and cyclohexanol. Reaction conditions: 10 mmol ether, 80 mL water, 20 mg 0.25 wt.% Ru/C, 40 bar of H₂ at room temperature, 150°C.
Figure S13. Time-yield plots (A), conversion-yield plots (B) and distributions of the reaction pathways plots (C) for the reaction of diphenyl ether on Rh catalyst in water. In (B), C₆ represents benzene, cyclohexene, and cyclohexane; C₆-OH represents phenol, cyclohexanone and cyclohexanol. Reaction conditions: 10 mmol ether, 80 mL water, 10 mg 0.25 wt.% Rh/C, 40 bar of H₂ at room temperature, 150°C.
Figure S14. Time-yield plots (A), conversion-yield plots (B) and distributions of the reaction pathways plots (C) for the reaction of diphenyl ether on Pd catalyst in water. In (B), C₆ represents benzene and cyclohexane; C₆-OH represents phenol, cyclohexanone, and cyclohexanol. Reaction conditions: 10 mmol ether, 80 mL water, 10 mg 5 wt.% Pd/C, 40 bar of H₂ at room temperature, 150°C.
Figure S15. Time-yield plots (A), conversion-yield plots (B) and distributions of the reaction pathways plots (C) for the reaction of diphenyl ether on Pt catalyst in water. In (B), C₆ represents benzene and cyclohexane; C₆-OH represents phenol, cyclohexanone, and cyclohexanol. Reaction conditions: 10 mmol ether, 80 mL water, 10 mg 5 wt.% Pt/C, 40 bar of H₂ at room temperature, 150°C.
Table S2. Kinetic isotopic results of diphenyl ether.^[a]

| Catalyst | Gas | TOF s\(^{-1}\) |
|----------|-----|----------------|
|          |     | Hydrogenolysis |
| Ru       | H\(_2\) | 0.041 |
|          | D\(_2\) | 0.06 |
| R\(_{H}/R_D\) |       | 0.7 |
| Rh       | H\(_2\) | 0.11 |
|          | D\(_2\) | 0.15 |
| R\(_{H}/R_D\) |       | 0.7 |
| Pd       | H\(_2\) | 0.005 |
|          | D\(_2\) | 0.006 |
| R\(_{H}/R_D\) |       | 0.8 |
| Pt       | H\(_2\) | 0.48 |
|          | D\(_2\) | 0.48 |
| R\(_{H}/R_D\) |       | 1.0 |

^a Reaction conditions: 10 mmol ether, 10 mg 5 wt.% Ru/C, 20 mg 0.25 wt.% Rh/C or 10 mg 5 wt.% Pd/C catalyst, 40 mL decalin, 5 bar of H\(_2\) or D\(_2\) at room temperature, 150°C, stirring at 700 ppm. TOFs were calculated at <20 % conversion.

Table S3.[^7] Turnover frequencies (TOFs) and reaction pathway selectivities at high conversion of the Pd/C-catalyzed transformation of diphenyl ether in various alcohols or in decalin as solvent.[^a]

| Solvent   | TOF / s\(^{-1}\) | Carbon selectivity / %[^b] |
|-----------|-----------------|----------------------------|
|           |                 | Hydrogenolysis | Solvolysis | Hydrogenation |
| Water     | 2.9             | 2 ±1           | 88 ±2       | 10 ±2         |
| Methanol  | 0.06            | 2 ±1           | 72 ±2       | 26 ±2         |
| Ethanol   | 0.21            | 4 ±2           | 47 ±5       | 49 ±5         |
| 1-Propanol| 0.35            | 4 ±2           | 44 ±5       | 52 ±5         |
| 2-Propanol| 1.6             | 6 ±2           | 32 ±5       | 62 ±5         |
| Decalin   | 1.0             | 3 ±1           | -           | 97 ±1         |

[^a]Reaction conditions: 20 mg 5 wt.% Pd/C (2.9 × 10\(^{-6}\) mol of Pd\(_{surf.}\)) or 20 mg 0.2 wt.% Pd/C (1.2 × 10\(^{-7}\) mol of Pd\(_{surf.}\)), solvent (80 mL), diphenyl ether (1 mmol), H\(_2\) (40 bar gauge pressure at room temperature), temperature (200 °C) and stirring (700 rpm). TOFs were calculated from conversions of <20 %.[^b] Caculated at > 90 % conversion: hydrogenolysis = 2 × (cyclohexane + benzene); solvolysis = (cyclohexyl-OR + cyclohexanol + phenol + cyclohexanone + cyclohexenyl-OR + acetal) - hydrogenolysis; hydrogenation = (cyclohexyl phenyl ether + dicyclohexyl ether).
Table S4. TOFs of diphenyl ether and selectivities of different reaction routes over Ru/C.

| Solvent | KOH / mM | Temp. / °C | H₂ / bar | TOF / s⁻¹ | Selectivity / % | Hydrogenation | Hydrogenolysis | Hydrolysis |
|---------|----------|------------|----------|------------|-----------------|---------------|---------------|-----------|
| Water   | 200      | 4          | 0.5      | 7          | 90              | 3             |               |           |
| Water   | 200      | 40         | 16.1     | 46         | 48              | 7             |               |           |
| Water   | 150      | 40         | 5.7      | 69         | 20              | 11            |               |           |
| Water   | 100      | 40         | 0.9      | 76         | 10              | 14            |               |           |
| Water 1 | 200      | 40         | 11.5     | 39         | 56              | 5             |               |           |
| Water 10| 200      | 4          | 0.4      | 4          | 94              | 2             |               |           |
| Water 10 mM KBr | 200 | 40         | 12.8     | 45         | 49              | 6             |               |           |
| Water   | 150      | 40         | 2.0      | 79         | 21              | 11            |               |           |
| Water   | 100      | 40         | 0.3      | 85         | 15              |               |               |           |

Reaction conditions: Diphenyl ether (1.70 g), 5 wt.% Ru/C (10.0 mg), water (80 mL) or decalin (40 mL), 100~200°C, 4 or 40 bar of H₂ at room temperature, pH = 7~13, stirring at 700 rpm.

Table S5. TOFs of diphenyl ether and selectivities of different reaction routes over Rh/C.

| Solvent | KOH / mM | Temp. / °C | H₂ / bar | TOF / s⁻¹ | Selectivity / % | Hydrogenation | Hydrogenolysis | Hydrolysis |
|---------|----------|------------|----------|------------|-----------------|---------------|---------------|-----------|
| Water   | 200      | 4          | 2.5      | 43         | 53              | 4             |               |           |
| Water   | 200      | 40         | 140      | 78         | 13              | 9             |               |           |
| Water   | 150      | 40         | 29       | 82         | 5               | 13            |               |           |
| Water   | 100      | 40         | 2.8      | 91         | 2               | 7             |               |           |
| Water 10| 200      | 40         | 25       | 74         | 22              | 4             |               |           |
| Water 10| 200      | 4          | 0.5      | 29         | 68              | 3             |               |           |
| Decalin | 150      | 40         | 7.4      | 91         | 9               |               |               |           |
| Decalin | 100      | 40         | 1.0      | 94         | 6               |               |               |           |

Reaction conditions: diphenyl ether (1.70 g), 0.25 wt.% Rh/C (20.0 mg), water (80 mL) or decalin (40 mL), 100~200°C, 4 or 40 bar of H₂ at room temperature, pH = 7 or 12, stirring at 700 rpm.

Table S6. TOFs of diphenyl ether and selectivities of different reaction routes over Pd/C.

| Solvent | KOH / mM | Temp. / °C | H₂ / bar | TOF / s⁻¹ | Selectivity / % | Hydrogenation | Hydrogenolysis | Hydrolysis |
|---------|----------|------------|----------|------------|-----------------|---------------|---------------|-----------|
| Water   | 200      | 4          | 0.27     | 54         | 24              | 21            |               |           |
| Water   | 200      | 40         | 2.8      | 65         | 3               | 33            |               |           |
| Water   | 150      | 40         | 0.64     | 81         | 2               | 17            |               |           |
| Water   | 100      | 40         | 0.033    | 85         | 1               | 15            |               |           |
| Water 10| 200      | 40         | 0.59     | 84         | 7               | 9             |               |           |
| Water 10| 200      | 40         | 0.14     | 72         | 13              | 15            |               |           |
| Water 10| 200      | 4          | 0.5      | 59         | 29              | 12            |               |           |
| Decalin | 150      | 40         | 0.70     | 98         | 2               |               |               |           |
| Decalin | 100      | 40         | 0.05     | 99         | 1               |               |               |           |

Reaction conditions: diphenyl ether (1.70 g), 5 wt.% Pd/C (10.0 mg), water (80 mL) or decalin (40 mL), 100~200°C, 4 or 40 bar of H₂ at room temperature, pH = 7~13, stirring at 700 rpm.
Table S7. TOFs of diphenyl ether and selectivities of different reaction routes over Ir/C.

| Solvent | KOH/mM | Temp./°C | H₂ / bar | TOF / s⁻¹ | Hydrogenation | Hydrogenolysis | Hydrolysis |
|---------|--------|----------|----------|-----------|---------------|----------------|------------|
| Water   | 200    | 4        |          | 3.7       | 51            | 44             | 5          |
| Water   | 200    | 40       |          | 49.6      | 70            | 23             | 7          |
| Water   | 150    | 40       |          | 11.6      | 67            | 22             | 11         |
| Water   | 100    | 40       |          | 0.49      | 89            | 8              | 3          |
| Water   | 10     | 200      | 40       | 3.6       | 61            | 34             | 5          |
| Water   | 10     | 100      | 40       | 0.4       | 38            | 60             | 2          |
| Decalin | 100    | 40       |          | 0.3       | 91            | 9              | -          |
| Decalin | 150    | 40       |          | 5.5       | 80            | 20             | -          |

Reaction conditions: diphenyl ether (1.70 g), 5 wt.% Pt/C (10.0 mg), water (80 mL) or decalin (40 mL), 100~200°C, 4 or 40 bar of H₂ at room temperature, pH = 7 or 12, stirring at 700 rpm.

Table S8. TOFs of diphenyl ether and selectivities of different reaction routes over Pt/C.

| Solvent | KOH/mM | Temp./°C | H₂ / bar | TOF / s⁻¹ | Hydrogenation | Hydrogenolysis | Hydrolysis |
|---------|--------|----------|----------|-----------|---------------|----------------|------------|
| water   | 200    | 4        |          | 3.7       | 51            | 44             | 5          |
| water   | 200    | 40       |          | 49.6      | 70            | 23             | 7          |
| water   | 150    | 40       |          | 11.6      | 67            | 22             | 11         |
| water   | 100    | 40       |          | 0.49      | 89            | 8              | 3          |
| water   | 10     | 200      | 40       | 3.6       | 61            | 34             | 5          |
| water   | 10     | 100      | 40       | 0.4       | 38            | 60             | 2          |
| decalin | 100    | 40       |          | 0.3       | 91            | 9              | -          |
| decalin | 150    | 40       |          | 5.5       | 80            | 20             | -          |

Reaction conditions: diphenyl ether (1.70 g), 5 wt.% Pt/C (10.0 mg), water (80 mL) or decalin (40 mL), 100~200 °C, 4 or 40 bar of H₂ at room temperature, pH = 7 or 12, stirring at 700 rpm.
Table S9. Activation energies of different reaction pathways on different metals in water.

|        | Hydrogenation | Hydrogenolysis | Hydrolysis |
|--------|---------------|----------------|------------|
| Ru     | 35 ±10        | 65 ±10         | 33 ±10     |
| Rh     | 55 ±3         | 85 ±3          | 62 ±10     |
| Pd     | 62 ±15        | 77 ±15         | 82 ±15     |
| Pt     | 65 ±7         | 82 ±25         | 84 ±17     |

Reaction conditions: 10 mmol ether, 10 mg 5 wt.% Ru/C, 20 mg 0.25 wt.% Rh/C, 10 mg 5 wt.% Pd/C or 20 mg 0.25 wt.% Pt/C catalyst, 80 ml water, 40 bar of H₂ at room temperature, 100–200°C, stirring at 700 rpm. TOFs were calculated at <20 % conversion.

Table S10. Activation energies of different reaction pathways on different metals in decalin.

|        | Hydrogenation | Hydrogenolysis |
|--------|---------------|----------------|
| Ru     | 48 ±4         | 61 ±2          |
| Rh     | 58 ±4         | 62 ±22         |
| Pd     | 69 ±2         | 94 ±5          |
| Ir     | 28 ±1         | 39 ±1          |
| Pt     | 76 ±2         | 97 ±13         |

Reaction conditions: 10 mmol ether, 10 mg 5 wt.% Ru/C, 20 mg 0.25 wt.% Rh/C, 10 mg 5 wt.% Pd/C, 10 mg 5 wt.% Ir/C or 20 mg 0.25 wt.% Pt/C catalyst, 80 ml decalin, 40 bar of H₂ at room temperature, 100-170°C, stirring at 700 rpm. TOFs were calculated at <20 % conversion.
Table S11. Comparison of the reactivity and the selectivity of different reaction pathways of diphenyl ether on commercial and self-made Ru, Rh, Pt and Pd catalysts.\(^a\)

| Catalyst       | Rates / \(\text{mol mol}^{-1}\text{s}^{-1}\) | Selectivity / % |
|----------------|---------------------------------------------|------------------|
|                | Hydrogenation | Hydrogenolysis | Hydrolysis |
| 5 wt.% Ru/C    | 16.1\(^b\)  | 46             | 48         | 7          |
| 5 wt.% Rh/C    | 140\(^b\)    | 78             | 13         | 9          |
| 5 wt.% Pd/C    | 2.8\(^b\)    | 63             | 3          | 34         |
| 5 wt.% Pt/C    | 49.6\(^b\)   | 70             | 23         | 7          |
| 0.5 wt.% Ru/C-R200\(^d\) | 2.1\(^c\) | 47             | 37         | 16         |
| 0.5 wt.% Rh/C-R200\(^d\) | 1.1\(^c\) | 68             | 12         | 20         |
| 1.0 wt.% Pd/C-R200\(^d\) | 0.5\(^c\) | 61             | 6          | 33         |
| 1.0 wt.% Pt/C-R200\(^d\) | 5.2    | 62             | 17         | 21         |
| 0.5 wt.% Ru/C-R300\(^e\) | 1.7\(^c\) | 46             | 38         | 16         |
| 0.5 wt.% Rh/C-R300\(^e\) | 0.4\(^c\) | 64             | 15         | 21         |
| 1.0 wt.% Pd/C-R300\(^e\) | 0.3\(^c\) | 56             | 6          | 33         |
| 1.0 wt.% Pt/C-R300\(^e\) | 1.2\(^c\) | 71             | 14         | 14         |
| 0.5 wt.% Ru/C-R450\(^f\) | 1.7\(^c\) | 44             | 41         | 15         |
| 0.5 wt.% Rh/C-R450\(^f\) | 0.3\(^c\) | 63             | 15         | 22         |
| 1.0 wt.% Pd/C-R450\(^f\) | 0.06\(^c\) | 63             | 13         | 24         |
| 1.0 wt.% Pt/C-R450\(^f\) | 0.1\(^c\) | 66             | 21         | 14         |

\(^a\) Reaction conditions: 10 mmol ether, 80 mL water, 10 mg 5 wt.% metal/C or 50 mg ~1 wt.% metal/C, 40 bar of \(\text{H}_2\) at room temperature, 200°C. TOFs were calculated at <20 % conversion.

\(^b\) Calculated from conversions <20 % and based on the number of surface metal atoms measured by \(\text{H}_2\) chemisorption.

\(^c\) Calculated from conversions <20 % and based on the number of total metal atoms measured by ICP-AES.

\(^d\) Catalysts were pre-reduced at 200°C.

\(^e\) Catalysts were pre-reduced at 300°C.

\(^f\) Catalysts were pre-reduced at 450°C.

Table S12. Particle sizes and dispersions calculated from particle size and \(\text{H}_2\) chemisorption of noble metal catalysts.

| Catalyst       | Particle size / nm | Dispersion (TEM)\(^[8]\) | Dispersion (chemisorption) |
|----------------|--------------------|--------------------------|---------------------------|
| 5 wt.% Ru/C    | 5.2                | 20%                      | 23%                       |
| 5 wt.% Rh/C    | 5.8                | 19%                      | 27%                       |
| 5 wt.% Pd/C    | 3.1                | 34%                      | 31%                       |
| 5 wt.% Ir/C    | 5.3                | 21%                      | 22%                       |
| 5 wt.% Pt/C    | 3.2                | 35%                      | 57%                       |

Dispersions from \(\text{H}_2\) chemisorption measurements are slightly higher than dispersions calculated from particle sizes except for Pd. This might be caused by small nanoparticles that could not be detected by the TEM measurements. Therefore, TOFs were calculated based on the number of surface metal atoms measured by \(\text{H}_2\) chemisorption.
Table S13. Selectivities of different reaction routes of diphenyl ether over different metal catalysts in decalin and water at full conversions.

| Solvent | Catalyst | Time/min | Conversion | Hydrogenolysis | Hydrolysis | Hydrogenation |
|---------|----------|----------|------------|----------------|------------|--------------|
| Decalin | 5 wt.% Ru/C | 180 | 100% | 21% | 79% |
|        | 5 wt.% Rh/C | 60 | 99% | 11% | 89% |
|        | 5 wt.% Pd/C | 360 | 98% | 2% | 98% |
|        | 5 wt.% Ir/C | 360 | 99% | 25% | 75% |
|        | 5 wt.% Pt/C | 660 | 97% | 19% | 81% |
| Water  | 5 wt.% Ru/C | 60 | 99% | 22% | 42% | 36% |
|        | 5 wt.% Rh/C | 60 | 100% | 8% | 42% | 50% |
|        | 5 wt.% Pd/C | 360 | 100% | 2% | 84% | 14% |
|        | 5 wt.% Pt/C | 300 | 99% | 32% | 18% | 50% |

Reaction conditions: 10 mmol ether, 10 mg catalyst, 40 mL decalin or 80 mL water, 40 bar of H₂ at room temperature, 150°C, stirring at 700 ppm.

Table S14: H₂ adsorption equilibrium constants $K_{H₂,ads.}$ at 150°C and ratio of TOF(hydrogenolysis)/TOF(hydrogenation).

| Metal | $K_{H₂,ads.}$ at 150°C | TOF(hydrogenolysis)/TOF(hydrogenation) |
|-------|------------------------|----------------------------------------|
|       |                        | 4 bar | 20 bar | 40 bar |
| Ru    | 2.9·10⁻⁶               | 1.1   | 0.44   | 0.27   |
| Rh    | 1.5·10⁻⁵              | 0.15  | 0.10   | 0.099  |
| Pd    | 2.5·10⁻⁵              | 0.048 | 0.028  | 0.020  |
| Ir    | 1.2·10⁻⁵              | 0.31  | 0.26   | 0.14   |
| Pt    | 3.3·10⁻⁶              | 0.64  | 0.35   | 0.25   |

TOF(hydrogenolysis)/TOF(hydrogenation) were determined from experimental data at 4 bar and 40 bar and calculated from extrapolated values at 20 bar from fits of the reaction orders in hydrogen of the different metals in decalin.
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