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The Critical Role of Reductive Steps in the Nickel-Catalyzed Hydrogenolysis and Hydrolysis of Aryl Ether C-O Bonds

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Abstract: Hydrogenolysis of the aromatic C-O bond in aryl ethers catalyzed by Ni was studied in decalin and water. Observations of a significant kinetic isotope effect ($k_H/k_D = 5.7$) for the reactions of diphenyl ether under H_2 and D_2 and a positive dependence of the rate on H_2 chemical potential in decalin indicate that addition of H to the aromatic ring is involved in the rate-limiting step. All kinetic evidence points to the fact that H addition occurs concerted with C-O bond scission. DFT calculations also suggest a route consistent with these observations involving hydrogen-atom addition to the ipso-position of the phenyl ring concerted with C-O scission. Hydrogenolysis initiated via H addition in water is more selective (~75 %) compared to reactions in decalin (~30 %).

Introduction

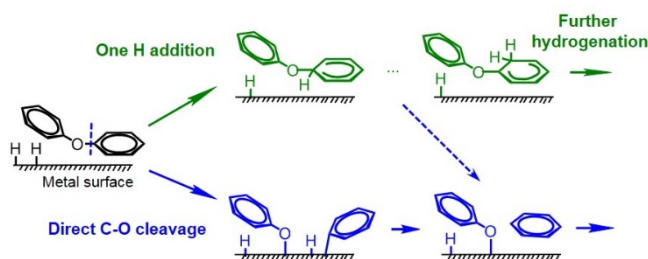
Activation of the aryl C-O bond in aromatic ethers is a necessary step for lignin depolymerization^[1] and a versatile synthetic strategy for cross-coupling of aryl groups.^[2] However, the reaction routes, i.e., hydrogenolysis and hydrolysis, as well as the competing hydrogenation routes (which saturate the aromatic rings without changing the molecular backbone) are challenging to control.^[3] Thus, selective aromatic C-O bonds cleavage is highly important for removing an oxygen-based directing group from an aryl ring as well as for synthesis of fuels and fine chemicals from biomass.^[4] Transition-metal catalysts, both heterogeneous and homogeneous, have been reported for oxidative and reductive cleavage of C-O bonds.^[2b, 5] Homogeneous and heterogeneous Ni catalysts selectively catalyze hydrogenolysis of aryl ethers in the liquid phase.^[4f, 6] Some mechanisms have been proposed to be initiated via C-O bond scission followed by H addition to the fragments.^[4b, 4c, 4f] Nevertheless, for heterogeneous catalysts, the high selectivity for hydrogenolysis and the high reactivity in polar and non-polar

phases,^[4d, 6b, 7] has not been explained by the accepted mechanisms.

Diphenyl ether has been widely used as model compound for the investigation of selective cleavage of aryl ether bond. Its symmetric structure simplifies products analysis, and the strong bond dissociation energy provides a challenging substrate for catalyst development.^[4d, 4f-h, 8] The pathways of reductive conversion of diphenyl ether (Ph_2O) have been broadly classified into hydrogenolysis, hydrogenation, and reductive hydrolysis.^[4g] For clarity, we consider hydrogenation to be the sequence of reactions that saturate the aromatic rings (i.e., cyclohexyl phenyl ether and dicyclohexyl ether), hydrogenolysis the reactions that produce C_6 hydrocarbons (e.g., benzene and cyclohexane) and C_6 oxygenates (e.g., phenol, cyclohexanone and cyclohexanol) in 1:1 ratio, and reductive hydrolysis the reactions that produce only C_6 oxygenates.

Because the catalytic reductive conversion of Ph_2O on heterogeneous catalysts always leads to a mixture of products from hydrogenolysis and hydrogenation,^[4a, 6b] the initial rate of H addition to the aromatic ring (upper route in Scheme 1) is comparable to, or even faster than the C-O bond scission (lower route in Scheme 1). This raises the question of whether the H addition occurs after the C-O bond scission, as reported in homogeneous catalysis.^[4f] Since we have discovered that the C-O bond in Ph_2O can be hydrolytically cleaved after partial hydrogenation of the aromatic ring on Pd^[4g, 4h], an alternative consideration is that hydrogenolysis of the aromatic C-O bond occurs concerted with or following hydrogen addition to the aromatic ring (dashed line in Scheme 1).

Scheme 1. Initial steps proposed for hydrogenation and hydrogenolysis of diphenyl ether on metal surface.



Here, we show the reaction paths on Ni/SiO₂ in polar (water) and non-polar (decalin) solvents in the presence of H_2 , combining kinetics (including isotope labelling) with density functional theory (DFT) calculations to derive a detailed molecular account of the reaction steps (Scheme 1). The results indicate that hydrogen addition to the aromatic ring is kinetically relevant to the hydrogenolysis route. The addition of H occurs at faster rates in decalin than in water without changes in the reaction mechanism, although lower apparent activation energies and higher selectivity to hydrogenolysis were observed in the aqueous phase than in decalin.

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Supporting information for this article is given via a link at the end of the document.

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Results and Discussion

The reaction conditions are described in the figure captions and table footnotes. Details for experimental procedures and DFT calculations are listed in the Supporting Information.

Powder XRD showed Ni to be present as crystalline metallic particles, and the fractional exposure of metal was 7 % by H₂ chemisorption measurement (see characterization details in SI). Ph₂O was fully converted after 10 hours in water (turnover number (TON) = 650) or after 4 hours in decalin (TON = 1300), while products from C-O cleavage, i.e., C₆ hydrocarbons and C₆ oxygenates, and hydrogenation, i.e., cyclohexyl phenyl ether (CyOPh) and dicyclohexyl ether (Cy₂O), were observed in either solvent (Figure 1). C₆ hydrocarbons (benzene and cyclohexane) and C₆ oxygenates (phenol, cyclohexanone and cyclohexanol). Cyclohexanol was a major constituent of the C₆ oxygenates, and the selectivities to benzene and cyclohexane varied over the course of the reaction (Figures S1 and S2), due to secondary reactions, i.e., the hydrogenolysis and hydrolysis of CyOPh and hydrogenation of phenol, cyclohexanone and benzene.

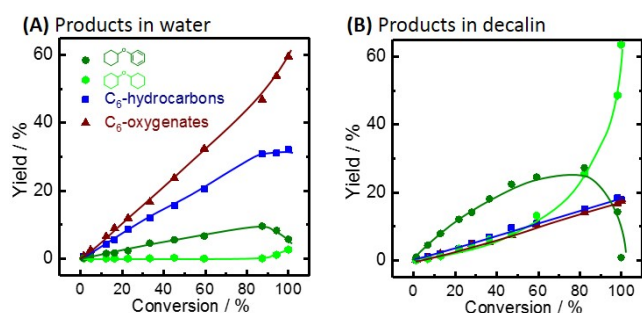


Figure 1. Product distributions as a function of conversion of diphenyl ether over Ni/SiO₂ in water (A) and decalin (B) under the same reaction conditions: diphenyl ether (1.70 g), 64 wt. % Ni/SiO₂ catalyst (20 mg in water and 10 mg in decalin), solvent (water 80 mL or decalin 40 mL), stirring at 700 rpm, reaction temperature is 150 °C and the H₂ pressure is about 59 bar. C₆-hydrocarbons represents benzene and cyclohexane, C₆-oxygenates represents phenol, cyclohexanone and cyclohexanol. The reactions in water and decalin were carried out for 10 and 4 hours respectively. The detailed time-yield plots and distributions of the reaction pathways are shown in Figure S1 and S2.

While the same products are produced in either water or decalin, the product distribution is substantially different. In water, C-O cleavage is the dominant reaction, and the selectivity of C₆

oxygenates exceeds the selectivity of C₆ hydrocarbons (Figure 1a). Since hydrogenolysis of Ph₂O generates equal amounts of phenol and benzene, the additional yield of C₆ oxygenates is attributed to hydrolysis of Ph₂O and CyOPh.^[49] The yields of CyOPh, C₆ oxygenates and C₆ hydrocarbons increased with time up to 90 % conversion of Ph₂O, after which the yield of CyOPh decreased while the yield of C₆ oxygenates increased, and the yield of C₆ hydrocarbons levelled off. This behavior indicates that the selectivity for hydrolysis increased when CyOPh was converted (Figure S1).

Reactions in decalin yielded predominantly hydrogenation products (CyOPh and Cy₂O). The C₆ oxygenates and C₆ hydrocarbons were produced in approximately equal amounts reflecting the absence of hydrolysis (Figure 1b). CyOPh was the major product at below 60 % conversion. Because CyOPh also underwent hydrogenolysis and hydrogenation, the overall selectivity of hydrogenolysis slightly increased from 29 % at low conversion to 35 % at full conversion (Figure S2).

To focus on the initial reactions of Ph₂O and minimize secondary reactions, we measured the TOFs of Ph₂O and the selectivity in water and decalin at conversions less than 20 % (Table 1). The selectivity to the three pathways, hydrogenolysis, hydrogenation, and hydrolysis, were calculated from the product distribution. In water, at 150 °C and 59 bar H₂ (Table 1, entry 1), the high selectivity to benzene (36 %) indicates that hydrogenolysis was the dominant reaction route (72 %). The selectivity to phenol (6 %) is lower than to benzene, because phenol was hydrogenated faster than benzene.^[6b] The overall higher selectivity (53 %) to C₆ oxygenates (6 % phenol, 4 % cyclohexanone, and 43 % cyclohexanol) than to C₆ hydrocarbons (mainly benzene) showed that hydrolysis also occurred to an extent of approximately 17 %. Ph₂O reacted five times faster in decalin (Table 1, entry 2, TOF = 830 h⁻¹) than in water (Table 1, entry 1, TOF = 140 h⁻¹) under the same conditions. Hydrogenation was the dominant reaction route (71 %) and only hydrogenolysis contributed to the minor products (29 %), since hydrolysis does not occur in the absence of water (equal amounts of C₆ oxygenates and C₆ hydrocarbons were produced). To study the effect of H₂ pressure on rate and selectivity, we also performed reactions at 17 and 6 bar H₂, (Table 1, entries 3 and 4). The four major products, i.e., benzene (5 – 16 %), cyclohexanol (13 – 20 %), CyOPh (56 – 61 %) and Cy₂O (2 – 10 %), were all obtained at all H₂ pressures (6 – 60 bar). Hydrogenation (58 % - 71 %) remained the dominant route even at the lowest H₂ pressure.

Table 1. Reactions of diphenyl ether on Ni/SiO₂ in water and decalin solvents under hydrogen gas.^[a]

Entry	Solvent	H ₂ / bar	TOF ^[b] / h ⁻¹	Products carbon selectivity / %							Reaction routes selectivity ^[c] / %		
											Hydrogenolysis	Hydrogenation	Hydrolysis
1	Water	58.6	140	36	-	6	4	43	11	-	72	11	17
2	Decalin	59.5	830	5	10	1	-	13	61	10	29	71	-
3	Decalin	17.3	290	16	2	1	-	16	57	8	35	65	-
4	Decalin	6.2	160	15	6	1	-	20	56	2	42	58	-

^[a] Reaction conditions: reactant (1.70 g), 64 wt. % Ni/SiO₂ catalyst (10 mg), solvent (water 80 mL or decalin 40 mL), 150 °C, stirring at 700 rpm. Hydrogen pressure was corrected to 150 °C (see details in SI) ^[b] Calculated at < 20 % conversion ^[c] hydrogenolysis = 2 × (cyclohexane + benzene); hydrolysis = (phenol + cyclohexanone + cyclohexanol) - hydrogenolysis; hydrogenation = (phenyl cyclohexyl ether + dicyclohexyl ether).

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Control experiments were performed with the initial products, benzene, phenol, and CyOPh, from Ph₂O to investigate the secondary reactions (Table S1). Compared to the TOF observed from Ph₂O (290 h⁻¹) at 150 °C and 17.3 bar of H₂ in decalin, the TOFs using phenol as a substrate were one order of magnitude higher in the presence (1700 h⁻¹) or absence (2100 h⁻¹) of Ph₂O; the TOFs of other initial products, CyOPh (110 h⁻¹) and benzene (120 h⁻¹), were comparable with Ph₂O. The fast hydrogenation of phenol explains its low yield in reactions of Ph₂O and CyOPh even though phenol is an initial product from hydrogenolysis of Ph₂O. In water, the rate of phenol conversion was also higher (660 h⁻¹) than that of Ph₂O (140 h⁻¹), whereas the rates of conversion of other small compounds were lower than that of Ph₂O.

In summary, the same products were formed in water and in decalin, though with different distributions. Hydrogenation and hydrogenolysis are significant routes in both solvents, while selectivity for hydrogenation is greater in decalin, in part because hydrolysis cannot occur. In what follows, we elucidate details of the reaction mechanism for hydrogenolysis.

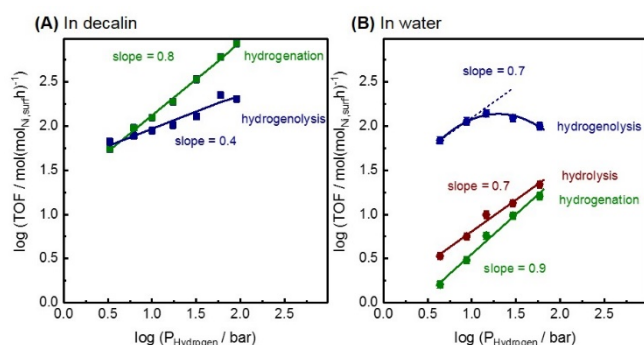


Figure 2. Hydrogen dependencies for the reactions of diphenyl ether over Ni/SiO₂ in decalin (A) and water (B). H₂ pressure varies from 3.3 to 90 bar in decalin and from 4.4 to 59 bar in water.

Table 2. Reaction rates and the corresponding isotope effects observed for the conversion of diphenyl ether with H₂ or D₂.^[a]

Gas	TOF / h ⁻¹		
	Hydrogenolysis	Hydrogenation	Deuteration ^[b]
H ₂	68 ± 5	95 ± 5	
D ₂	12 ± 3	20 ± 4	35 ± 5
KIE _{H/D}	5.7	4.8	

^[a] Reaction conditions: Diphenyl ether (1.70 g), 64 wt. % Ni/SiO₂ catalyst (10 mg), decalin 40 mL, 150 °C, gas pressure is 6.2 bar at 150 °C, stirring at 700 rpm. TOFs are calculated at < 20 % conversion. ^[b] Rate of the deuteration of diphenyl ether from the H/D exchange between diphenyl ether and D₂ (Figure S4). The deuteration at the *o*-, *m*- and *p*-positions were quantified by ²H NMR (Figure S8), the *o*:*m*:*p* distribution is 1 : 2 : 1.

Hydrogenolysis is favored by lower pressures of H₂ in decalin (Figure 2a). Commensurately, the reaction orders in H₂ for Ph₂O hydrogenolysis and hydrogenation were 0.4 and 0.8, respectively, in the pressure range 3.3 – 90 bar H₂ (Figure 2a). The constant and positive reaction order over a 27-fold variation in H₂ pressure indicates that the H surface coverage was relatively low under these conditions. The observation that hydrogenolysis was

approximately half order in H₂, while hydrogenation first order in H₂, suggests a mechanism in which one H atom is added before or during the rate determining step of the hydrogenolysis pathway.^[9] We rule out that H addition following C-O bond scission is rate determining, because hydrogen addition to the adsorbed fragments, i.e., phenyl or phenoxy, is rapid,^[10] and, thus, is not expected to limit the rate of hydrogenolysis.

To test the hypothesis that H-addition is rate-limiting for hydrogenolysis, deuterium kinetic isotope effects and tracer studies were performed in decalin, whence only hydrogenation and hydrogenolysis pathways occur and H/D exchange with D₂ is negligible. Reaction in water is not reported, because of the rapid exchange between D₂ and H₂O, D₂O with Ph₂O, and D₂O with reaction products. Consistent with the H₂ kinetic orders observed above, we measured significant kinetic isotope effects of 5.7 and 4.8 (Table 2) for hydrogenolysis and hydrogenation, respectively. This is perfectly reflected by our DFT-calculated *k_H*/*k_D* value of 5.7 for the Ni-H bond cleavage (see details in the supporting information). Thus, we conclude that hydrogen is involved in the rate determining step of the C-O bond scission.

To support the assignment of these effects to H-addition steps, we first note that H/D exchange between H₂ and D₂ equilibrated in the time interval required to reach reaction temperature (Figure S3). Thus, diffusion and activation of H₂/D₂ on the metal surface are concluded not to be rate-limiting steps. Secondly, even though H/D exchange occurred between D₂ and reactants/products, the abundance of D in D₂, HD, and H₂ (gas phase) never fell below 82 % (Figure S4). Conversions of the reactant in H/D exchange and reductive consumption were below 5 % (Figure S4). Lastly, the product distribution and selectivity were very similar for H₂ and D₂ (Figures S5 and S6). Therefore, initial rates of the hydrogenolysis and hydrogenation of Ph₂O are reliable measures of the isotope effects. We attribute the primary isotope effects to the cleavage of Ni-H versus Ni-D bonds in the transition states of rate-limiting steps for hydrogenolysis and hydrogenation.

For evidence that the kinetic isotope effect involves H addition to Ph₂O, we traced the positions into which D was incorporated in benzene, phenol, and unreacted Ph₂O. One D was found in benzene (C₆H₅D > 90 %) and no D was found in the aromatic ring of phenol (C₆H₅OD > 90%) (see Figure S7). Hence, the products from hydrogenolysis in D₂ are concluded to be C₆H₅D and C₆H₅OD (Figure S7). This indicates that only one H is added to the phenyl ring before or concerted with C-O bond scission.

The H/D exchange between Ph₂O and D₂ shows that H addition to the aromatic ring is reversible. The rates of H/D exchange (deuteration) are competitive with the rates of formation of the products (Table 2 and Figure S4). The distribution of D in the recovered Ph₂O is non-statistical, i.e., the proportion of D at *ortho*, *meta* and *para* positions is approximately 1:2:1 (Figure S8), respectively. This low level of D incorporation at the *ortho* position could indicate that the *o*-D-adduct is less favorably formed, or that the *o*-D-adduct is converted to products more rapidly than the *m*- and *p*-D-adducts. In support of the latter, density functional theory calculations (Table S2) find that the *o*- and *m*-H-adducts are energetically favored over the *p*-H-adduct by 17-18 kJ/mol, while the barriers to forming the *o*- and *p*-H-adducts are lower than the barrier to form the *m*-H-adduct by 13-14 kJ/mol. Addition of H to the carbon bonded to the OPh group (*ipso*-position) did not produce a stable surface-adsorbed H-adduct.

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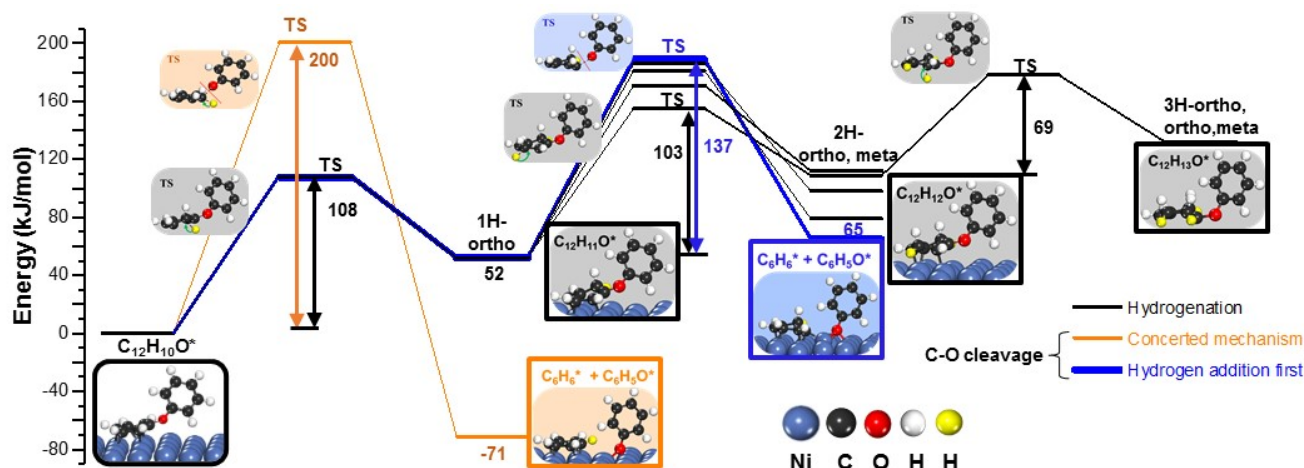


Figure 3. Potential energy profiles for hydrogenolysis and hydrogenation of diphenyl ether over Ni catalyst. A* represents the adsorption state of A on the surface. "Concerted mechanism" refers to C-O bond cleavage while a H is added to the phenyl ring and "Hydrogen addition first" means one hydrogen is added first, which is followed by C-O bond cleavage. Zero-point energy corrections have been applied to initial, transition and final states. White and yellow spheres are for H originally in diphenyl ether and H from metal surface.

An energy diagram calculated by DFT is shown in Figure 3 for hydrogenolysis and hydrogenation pathways (the corresponding structures are provided in Table S3). For hydrogenation, the stepwise addition of three hydrogen atoms via the initially formed *o*-H-adduct is shown. For hydrogenolysis, two routes are considered, i.e., (i) C-O bond breaking concerted with phenyl-H bond formation (H-assisted) and (ii) step-wise "hydrogen addition first (at *ortho* position)" followed by C-O bond cleavage. The concerted C-O bond breaking mechanism (orange line) has a higher activation barrier of 200 kJ/mol. Step-wise hydrogen-addition followed by C-O bond cleavage via the *o*-H-adduct has an overall barrier of 189 kJ/mol (black line) comprised of the energy of formation (52 kJ/mol) of *o*-H-adduct and the barrier (137 kJ/mol) for subsequent C-O bond scission. The concerted path initiated by *ipso* attack of a surface H atom is consistent with experimental observations of approximately half-order rate dependence on H₂ and a significant H₂/D₂ KIE. The stepwise route would be consistent, too, provided the back reaction of the H-adduct to Ph₂O (H-elimination) is competitive with C-O scission, which could be the case, if the frequency-factor for C-O scission is sufficiently greater than the frequency-factor for H-elimination. Thus, we do not exclude this route.

After the first hydrogen addition, the second H addition (103 – 133 kJ/mol) is, however, kinetically easier than the C-O bond scission (137 kJ/mol). Also, the third consecutive H addition step, with a low barrier of 69 kJ/mol, is feasible. This is consistent with the experimental observation of first order in H₂ for hydrogenation and the relatively high selectivity to hydrogenation products in decalin. The apparent activation energies for hydrogenolysis and hydrogenation in decalin were 101 and 77 kJ/mol, respectively (Figure S9). The higher activation enthalpy for hydrogenolysis compared to hydrogenation agrees well with the DFT calculations. In water, a different hydrogen dependence was observed for hydrogenolysis. Although the relations between the logarithmic rates of hydrogenation and hydrolysis and the logarithm of H₂ pressure were linear with slopes of 0.9 and 0.7, respectively, over

the H₂ pressure range of 4.4 – 59 bar (Figure 2b), the dependence of the logarithm of the hydrogenolysis rate on the logarithm of H₂ pressure was not. The H₂ dependence for hydrolysis, near 1st order, is similar to that observed on Pd catalysts.^[49] Thus, we hypothesize that hydrolysis is initiated by partial hydrogenation of Ph₂O to the enol ether, cyclohex-1-enyl phenyl ether, which converts to phenol and cyclohexanone. For hydrogenolysis over the range of 4.4–15 bar H₂, the TOF increased, and then decreased above 29 bar. Initially, the reaction order in H₂ is like that for hydrolysis, indicating that hydrogen is transferred to Ph₂O before or concerted with the C-O bond cleavage.

The reasons for the reaction order in H₂ to turn negative above 15 bar is unclear at present. Hydrogen addition to carbon-carbon double bonds on Ni is usually structure insensitive,^[11] while hydrogenolysis of C-C bonds in hydrocarbons is structure sensitive.^[12] Thus, we hypothesize that C-O bond cleavage of the H-adduct of Ph₂O, which requires an adjacent vacant site, is also structure sensitive. We suggest that water may block this vacant site via competitive adsorption, while other sites are more readily saturated by H. Under the high pressures of H₂, the reaction rate of hydrogenolysis decreases due to a decreasing concentration of H adduct-vacant site pairs, while hydrogenation and hydrolysis, which do not require an adjacent vacant site, still increase in rate with increasing H coverage (Figure S10).

Thus, hydrogenolysis follows the same mechanism in water and in decalin. Hydrogenolysis is initiated via H addition to the aromatic ring, which weakens the aromatic C-O bond. When the reactivities in decalin and water are compared under low H₂ pressures (3.3 – 15 bar), hydrogenation rates are much slower in water, while hydrogenolysis rates are comparable. This is attributed to a lower surface coverage of H in water than in decalin. In contrast, the dissociation of the polar ether C-O bond on Ni in water is more favorable due to stabilization of the transition state. Both compensating effects are, therefore, hypothesized to cause the high selectivity of hydrogenolysis in water.

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Conclusion

Thus, the high primary kinetic isotope effect ($KIE_{H/D} > 5$), the H_2 pressure dependence for Ni/SiO₂ catalyzed hydrogenolysis of diphenyl ether, and the DFT modeled routes, corroborate that the hydrogenolytic C-O bond cleavage of an aromatic ether bond on the surface of a Ni particle is initiated by hydrogen addition to the aromatic ring. This mechanism is in stark contrast to reaction routes that are catalyzed by molecular catalysts, where hydrogenolysis is initiated by a rate-determining oxidative addition of aryl ethers to neutral Ni⁰[4f]. The first step of hydrogen addition is followed by the ether C-O bond cleavage, which leads to benzene and phenoxyl groups on the metal surface. The present results also indicate that the partial hydrogenation of aromatic rings may be a more general reaction principle for cleaving C-O bonds in alcohols and ethers. This insight, in turn, opens new synthesis pathways enabling selective manipulation of C-O bonds currently explored.

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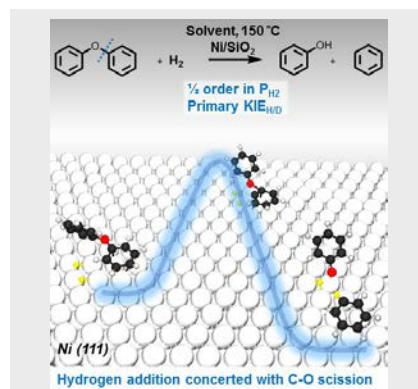
Keywords: nickel • catalysis • hydrogenolysis • reaction mechanism • selective cleavage

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A significant deuterium kinetic isotope effect ($k_H/k_D = 5.7$) for hydrogenolysis of diphenyl ether on Ni and a positive dependence of the rate on H_2 chemical potential point to a mechanism modeled by DFT in which cleavage of the aromatic ether bond is concerted with *ipso*-H-addition to the phenyl ring.



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The Critical Role of Reductive Steps in the Nickel-Catalyzed Hydrogenolysis and Hydrolysis of Aryl Ether C-O Bonds