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Hydrogenolysis of biomass derived aromatic ethers under lignin-first conditions

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Abstract

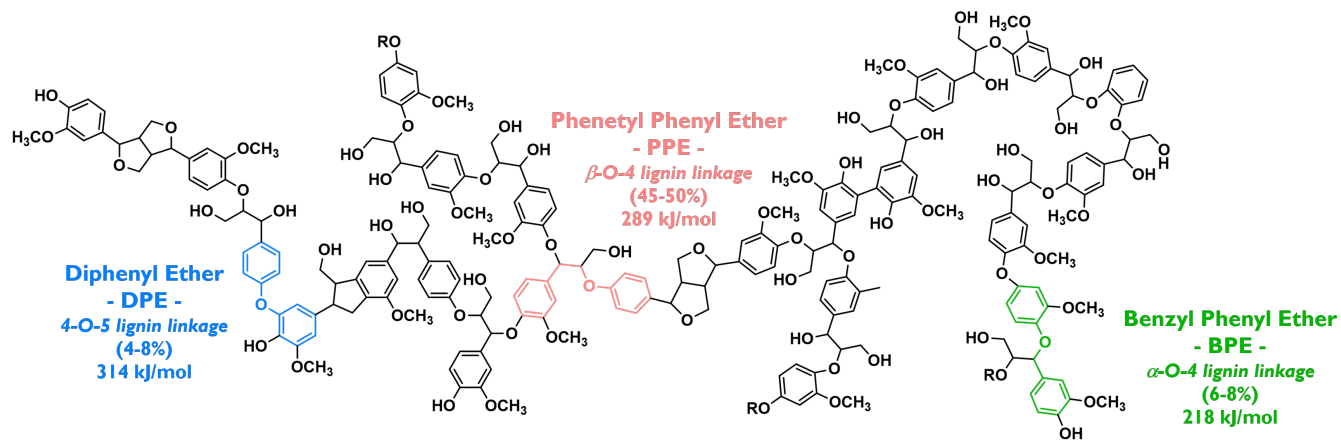
The cleavage of the etheric C-O bond in diphenyl ether (DPE), phenethyl phenyl ether (PPE) and benzyl-phenyl ether (BPE) has been investigated by using Ru/C and Pd/C, as heterogeneous catalysts, under reaction conditions generally adopted for the reductive catalytic fractionalization of lignocellulosic biomasses (**lignin-first** approach). Catalytic tests were carried out in the presence of simple C1-C3 alcoholic H-donor solvents (methanol, ethanol and 2-propanol) used as such or in mixture with water in the temperature range of 120–240°C both in the presence or in the absence of molecular hydrogen as reducing agent. **Under transfer hydrogenolysis conditions**, the Ru/C catalyst was found to be the best performing system in the cleavage of the 4–O–5 etheric C–O bond (**95% DPE conversion in 2-propanol at 210°C after 3 hours**) with a less pronounced tendency in hydrogenating the aromatic ring. Upon increasing the water content, a decrease in the cleavage of the C–O bond of DPE together with a higher production of phenolics is observed as a consequence of the reductive hydrolysis reaction occurrence. The best yield in aromatic compounds (**52%**) was obtained by using as solvent a water/2-propanol (75:25, v/v) mixture in absence of added molecular hydrogen, with the alcoholic fraction being the **in-situ** H-source. A lower tendency to undergo to hydrolysis reaction together with a higher production of aromatics registered in the case of phenethyl phenyl ether and benzyl-phenyl ether. Results are explained in terms of the higher steric hindrance of PPE and BPE with respect to DPE and of the competitive adsorption of arenes arising from hydrogenolysis of etheric β -O-4 and α -O-4 bonds (phenol + ethyl benzene or phenol + toluene) on the Ru/C catalyst surface.

1. Introduction

The time to put the old saying "you can make anything from lignin except money" in the attic has now come. While cellulose and hemicellulose already represent well established feedstocks for the production of several chemical commodities [1–4], only in the last years we have witnessed an effective use of lignin for the production of aromatic compounds [5, 6].

Owing to the improvement of reductive catalytic fractionalization (RCF) processes (also known as **lignin-first** approach) [7–9], a complete valorization of lignocellulosic biomasses into value-added chemicals, renewable energy and biofuels is firmly established today [10–12_REF Angela]. An integrated biorefinery based on the **lignin-first** approach, that can efficiency transform birch wood into xylochemicals, was recently reported opening a new era for the sustainable production of aromatics from lignocellulosic wastes and residues [13]. By using such a kind of reductive catalytic processes, the three key components of lignocellulosic biomass (cellulose ~40 wt %, hemicellulose ~25 wt % and lignin ~20 wt %) can be converted into bioethanol and phenolic monomers/oligomers.

In RCF processes, lignin is primary extracted from the lignocellulose by using an organic solvent (generally short-chain C1-C4 aliphatic alcohols or cycle ethers) adopted as such or in combination with water and successively depolymerized, under relative mild reaction conditions (180–250 °C for 2–6 h), in the presence of a direct (molecular H₂) or indirect (H-donor molecule/solvent) reducing agent and a heterogeneous redox-active catalyst (Pd/C and Ru/C being the most used [14–17]) that plays also a crucial role in the stabilization of phenolic units. The basic chemistry/catalysis beyond the depolymerization of lignin in RCF processes involves the lysis of C–O and C–C bonds in the presence (hydrogenolysis) or in the absence (transfer hydrogenolysis) of added molecular hydrogen. Indeed, hydrogenolysis and transfer hydrogenolysis (CTH) reactions represent a wide area in the valorization of lignocellulosic biomasses and their derived bio-based molecules [18–21].



Scheme 1. Simplest aromatic ethers generally adopted in order to mimic α -O-4, β -O-4, 4-O-5 lignin linkages [22–25].

With respect to lignin model molecules, diphenyl ether (DPE), phenethyl phenyl ether (PPE) and benzyl-phenyl ether (BPE) were largely used to study the cleavage of etheric 4-O-5, β -O-4 and α -O-4 bonds, respectively (Scheme 1) [26–38]. DPE mimics the most resistant etheric lignin linkages (bond dissociation energy of 315 kJ/mol), PPE is the most abundant etheric substructure of lignin (bond dissociation energy of 290 kJ/mol) while BPE represents the typical lignin-carbohydrate bond (bond dissociation energy of 220 kJ/mol) that needs to be broken in order to extract the lignin from the lignocellulosic matrix.

While several important contributions are based on the hydrogenolysis of DPE, PPE and BPE under classic hydrogenolysis and transfer hydrogenolysis conditions in aqueous or alcoholic solvents over monometallic and bimetallic heterogeneous catalysts, very few contributions are present in the literature on the C-O bond breaking of lignin model molecules under reductive catalytic fractionalization conditions [39–41]. In this context, it is worth to underline that the presence of water as co-solvent in RCF reactions can deeply influence the catalytic process playing a crucial role in (i) lowering the hydrogen solubility in reaction media, (ii) promoting the hydrolysis reaction and (iii) competing with the aromatic ethers adsorption occurrence on catalysts active sites [42, 43].

In this contribution we aim to investigate the molecular catalysis occurring in the **lignin-first** upgrading of lignocellulosic biomasses, by using commercially available Ru/C and Pd/C catalysts for the C-O bond cleavage of lignin model aromatic ethers (DPE, PPE and BPE). A detailed study on the effect of the water content in water/organic mixture solvent media on the conversion of aromatic ethers and in driving the products selectivity is also presented.

2. Experimental Section

2.1 Investigated Catalysts

All chemicals were purchased from commercial source and used without further purification. Ru/C (**with nominal ruthenium loading of 5 wt%**) and Pd/C (**with nominal palladium loading of 5 wt%**) catalysts were acquired from Sigma-Aldrich (Merck Life Science S.r.l.) and used after H₂ flow (**1 mL/min**) reduction (Ru/C: 350°C for 3 hours; Pd/C: 200°C for 2 hours). A complete physico-chemical characterization of commercial Ru/C and Pd/C catalysts was reported in the last years by some of the authors and from other research groups [44–46].

2.2 Catalytic Tests

Hydrogenolysis reactions were carried out in a 100 **mL** stainless steel autoclave (Parr Instruments Co.) at a stirring speed of 500 rpm. In a typical reaction, the reduced catalyst (0.1 g) suspended in a 0.1 M solution (40 **mL**) of the desired substrate in the chosen reaction solvent were poured into the reactor, which was purged three times with N₂ (99.99%) and subsequently pressurized at the desired initial H₂ or N₂ pressure. The system was heated from room temperature up to the **desired reaction temperature** (**heating rate of 5 °C/min**) and the temperature was monitored using a thermocouple fixed into the autoclave and connected to the reactor controller with the reaction time considered started when the reactor reached the set temperature that was kept constant for the required time. The range of operative conditions used for reactions was: 120–240°C, 10 bar initial H₂ or N₂ pressure, 30–360 min reaction time. At the end of the reaction, the reactor was cooled **in an ice bath** and, when at below room

temperature (20 °C), the pressure was released carefully and the liquid phase analysed using an off-line gas chromatograph (Agilent 6890N) equipped with a wide-bore capillary column (CP-WAX 52CB, 60 m, i.d. 0.53 mm) and a flame ionization detector (FID). The injector was settled at 250 °C and the temperature program started at 50 °C (held for 5 min) with the temperature raised to 240 °C at 2 °C/min (held for 60 min) and finally to 250 °C (held for 5 min) during the post run. In recycling tests, after any run, the catalyst was first recovered, then carefully washed with fresh 2-propanol and reused under the same reaction conditions.

When water was used as reaction (co-)solvent, products were extracted with ethyl acetate (eventual water traces were removed by adding anhydrous sodium sulfate to the organic phase).

Tetradecane was used as external standard to determine the liquid product concentration and carbon balance (better than $95 \pm 3\%$ for all reported experiments). When necessary, cross-check GC/MS analyses were carried out using a Thermo Fisher gas chromatograph apparatus (Trace 1310) equipped with a single-quadrupole mass spectrometer (ISQ LT).

The conversion (%), product selectivity (%), product yield (%) and aromatic yield (%) in the liquid phase were calculated on the basis of the following equations:

$$\text{Conversion [\%]} = \frac{\text{mol of reacted substrate}}{\text{mol of substrate feed}} \times 100 \quad (1)$$

$$\text{Liquid phase selectivity [\%]} = \frac{\text{mol of specific product in liquid phase}}{\text{sum of mol of all products in liquid phase}} \times 100 \quad (2)$$

$$\text{Product Yield [\%]} = \frac{\text{mol of specific product}}{\text{mol of substrate feed}} \times 100 \quad (3)$$

$$\text{Aromatic Yield [\%]} = \frac{\text{mol of all aromatic products}}{\text{mol of substrate feed}} \times 100 \quad (4)$$

In reactions carried out by using diphenyl ether as starting substrate, the hydrogenolysis, hydrolysis and hydrogenation selectivity [%] was calculated according to Ref. [38].

$$\text{Hydrogenolysis [\%]} = 2 \times (\text{benzene} + \text{cyclohexene}) \quad (5)$$

$$\text{Hydrolysis [\%]} = (\text{phenol} + \text{cyclohexanone} + \text{cyclohexanol}) - \text{hydrogenolysis} \quad (6)$$

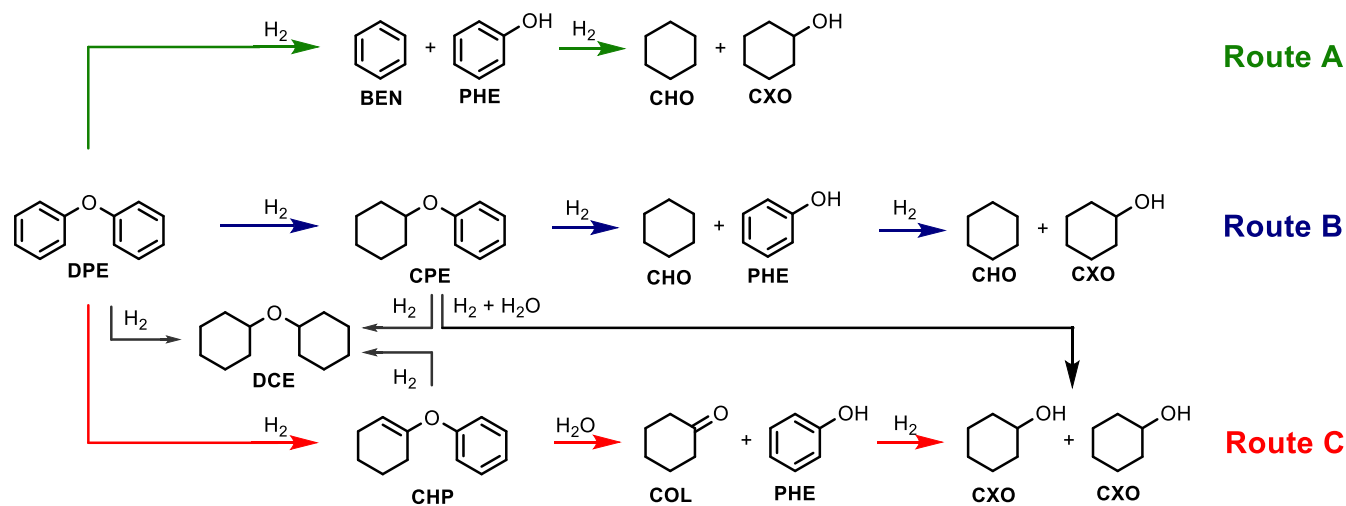
$$\text{Hydrogenation [\%]} = (\text{phenyl cyclohexyl ether} + \text{dicyclohexyl ether}) \quad (7)$$

3. Results and Discussion

3.1 Reaction pathways in the reductive upgrading of diphenyl ether under “lignin-first” conditions

Diphenyl Ether (DPE) can be considered the simplest lignin **model** molecule, therefore the cleavage of the etheric C–O bond in DPE is largely investigated as model reaction. In principle, under **lignin-first** conditions, the C–O bond cleavage of DPE may occur *via* three possible reaction routes (Scheme 2):

- route A (hydrogenolysis-hydrogenation pathway): the direct cleavage of the etheric C–O bond produces benzene and phenol that can be further hydrogenated into cyclohexane and cyclohexanol;
- route B (hydrogenation-hydrogenolysis pathway): the hydrogenation of DPE allows the production of cyclohexyl phenyl ether (rarely the full hydrogenation into dicyclohexyl ether was observed [32, 33]) that, in a successive hydrogenolysis reaction, is converted into phenol and cyclohexane;
- route C (reductive hydrolysis-hydrogenation pathway): DPE is partially hydrogenated into cyclohex-1-enyl phenyl ether (CHP) that, in presence of water, hydrolyzed rapidly forming equimolar amounts of cyclohexanone and phenol.



Scheme 2. Main reaction pathways in the reductive upgrading of diphenyl ether under **lignin-first** conditions

Route A and B are expected to occur both in water (hydrogenolysis conditions in presence of molecular H_2) as well as in organic H-donor solvents (CTH conditions) [47, 48]. In the case of the hydrogenation-hydrogenolysis pathway (Route B), it is worth to underline that, once DPE undergoes the hydrogenation of the aromatic ring without any C–O bond cleavage (with the concurrent formation of cyclohexyl phenyl ether), the hydrogenolysis of the benzylic $C(sp^3)$ –O bond is generally favored with respect to the aryl $C(sp^2)$ –O bond due to the minor dissociation energy involved. Obviously, route C can take place only when reactions are carried out in water although it was recently demonstrated that the presence of H_2 is a key prerequisite for the hydrolysis proceeding since H_2O cannot directly attack the etheric C–O bond of DPE [38].

3.2 Hydrogenolysis and transfer hydrogenolysis of diphenyl ether (DPE)

In order to gain a rapid catalysts screening and a preliminary insight on the solvent effect, the ability of Pd/C and Ru/C systems in the C–O bond cleavage in pure alcoholic solvents (2-PrOH, EtOH and MeOH) was explored both in the presence (hydrogenolysis conditions) and in the absence (transfer hydrogenolysis conditions) of added hydrogen (Table 1 and Fig. 1).

After 3 hours of reaction, under CTH conditions, a high DPE conversion at 210 °C (95%) can be obtained by using 2-PrOH as solvent/H-donor in the presence of Ru/C as catalyst. Benzene and cyclohexanol were obtained as main reaction products (selectivity of 37% and 40%, respectively) with an overall aromatic yield of 42%. A very low conversion (< 2%) was registered with ethanol and methanol. This result is not surprising considering the lower tendency of primary alcohols to undergo a dehydrogenation process with respect to secondary alcohols in releasing hydrogen species necessary for CTH reactions **as a consequence of their higher reduction potential as well as their smaller electron-releasing inductive effect** [35]. **Together with this, Vlacos and co-workers recently demonstrated that the hydrogenolysis of furfural is also correlated with solvent properties, such as polarity** [36].

Accordingly, higher DPE conversions can be easily achieved in the presence of molecular hydrogen as reducing agent for all investigated reaction solvents. By using Ru/C, the DPE conversion increases in the following order: methanol (85%), ethanol (95%), 2-PrOH (100%) in agreement with a report on the solvent effects on the hydrogenolysis of diphenyl ether promoted by Raney-Nickel catalyst [45]. However, under these reaction conditions, Ru/C catalyzes both hydrogenolysis of the ether bond as well as the hydrogenation of the aromatic ring with CHO and CXO being obtained in high yield.

Table 1. Hydrogenolysis of diphenyl ether promoted by Ru/C and Pd/C catalysts by using aliphatic C1-C3 alcohols (2-propanol, ethanol and methanol) or molecular hydrogen as H-source

Catalyst	Solvent	H-source	Conversion	Liquid Product Selectivity [%]						
			[%]	BEN	CHO	PHE	CXO	CON	CPE	DCE
Ru/C	2-PrOH	H ₂	100	-	50	-	50	-	-	-
Pd/C	2-PrOH	H ₂	100	4	42	-	52	-	-	2
Ru/C	2-PrOH	2-PrOH	95	37	12	7	40	-	4	-
Pd/C	2-PrOH	2-PrOH	45	19	21	13	22	7	16	2
Ru/C	EtOH	H ₂	95	5	36	3	37	1	18	

Pd/C	EtOH	H ₂	85	27	12	2	38	8	11	2
Ru/C	EtOH	EtOH	< 2	-	-	-	-	-	-	-
Pd/C	EtOH	EtOH	< 2	-	-	-	-	-	-	-
Ru/C	MeOH	H ₂	90	7	37	7	30	4	15	-
Pd/C	MeOH	H ₂	15	8	3	9	4	-	76	-
Ru/C	MeOH	MeOH	< 2	-	-	-	-	-	-	-
Pd/C	MeOH	MeOH	< 2	-	-	-	-	-	-	-

BEN: benzene; CHO: cyclohexane; PHE: phenol; CXO: cyclohexanol; CON: cyclohexanone; CPE: cyclohexyl phenyl ether; DCE: dicyclohexyl ether.

(reaction conditions: 40 mL of DPE 0.1 M; 0.100 g of catalyst; initial H₂ or N₂ pressure: 10 bar; reaction time: 3 hours; **reaction Temperature: 210°C**; speed stirring: 500 rpm.).

The commercial Pd/C generally exhibits a lower activity under both hydrogenolysis and CTH conditions if compared with the Ru/C catalyst (Table 1 and Fig. 1). Indeed, in absence of added hydrogen, a discrete DPE conversion was registered only in 2-PrOH (45%) while, by using EtOH and MeOH, as H-donor/reaction solvents, Pd/C is almost inactive. The modest performance of the commercial Pd/C catalyst in CTH reactions was already reported and attributed to its poor ability in dehydrogenating primary and secondary alcoholic H-donor-solvents with respect to other bimetallic Pd-based systems [37, 49, 50]. A better catalytic performance can be obtained under “classic” hydrogenolysis conditions with 2-propanol showing again an excellent performance in terms of DPE conversion (100%) together with a poor selectivity towards aromatic compounds. Interestingly, in the presence of molecular hydrogen, the formation of dicyclohexyl ether (DCE) - **rarely reported in reactions carried out under similar reaction conditions adopted in this paper** - among reaction products was registered.

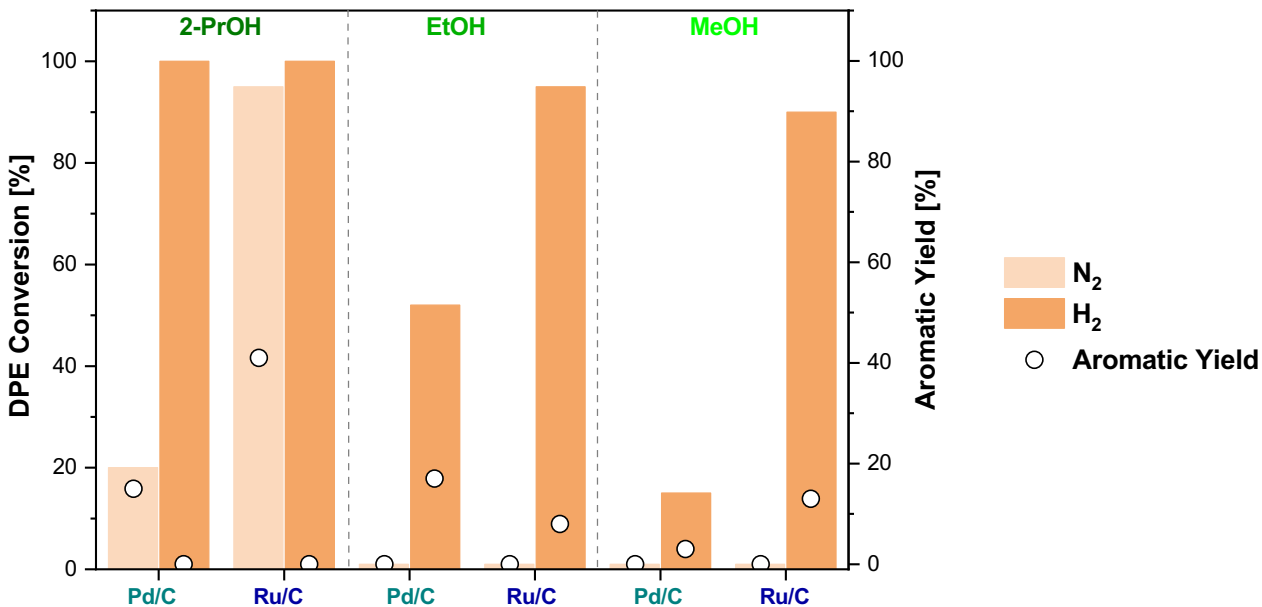


Fig. 1. CTH and hydrogenolysis of diphenyl ether promoted by Ru/C and Pd/C catalysts in pure alcoholic H-donor solvents (reaction conditions: 40 mL of DPE 0.1 M; 0.100 g of catalyst; initial H₂ or N₂ pressure: 10 bar; reaction time: 3 hours; reaction Temperature: 210°C; speed stirring: 500 rpm.)

It is worth to underline that the products distribution registered in reaction tests carried out in 2-PrOH in the absence of added hydrogen (BEN: 37%, CHO: 12%, PHE: 7%; CXO: 40%, CPE: 4%) and, in particular, the high selectivity in benzene suggest that the CTH of DPE mainly occurs through the primarily hydrogenolytic cleavage of the etheric 4–O–5 bond (Route A). At the same time, the detection of cyclohexyl phenyl ether, in liquid phase products, implies the simultaneous presence, in less extent, of the hydrogenation-hydrogenolysis pathway (Route B).

Whereas, the higher percentage of cyclohexyl phenyl ether (CPE) in reactions performed in presence of molecular hydrogen in EtOH and MeOH is clearly related to differences in the elementary steps of C–O bond cleavage implying that the different availability of hydrogen on the catalyst surface drives the hydrogenolysis reaction towards Route B. Therefore, the catalytic results clearly show that it is the availability of hydrogen that determines the route selectivity in the cleavage of etheric C–O bond [51].

3.3 Reaction time effect in the transfer hydrogenolysis reaction of DPE and the consequent kinetic model that can be derived

The preference of the hydrogenolysis-hydrogenation route in the CTH reaction was confirmed by monitoring yield and distribution of reaction products as a function of time at 210°C (Fig. 2).

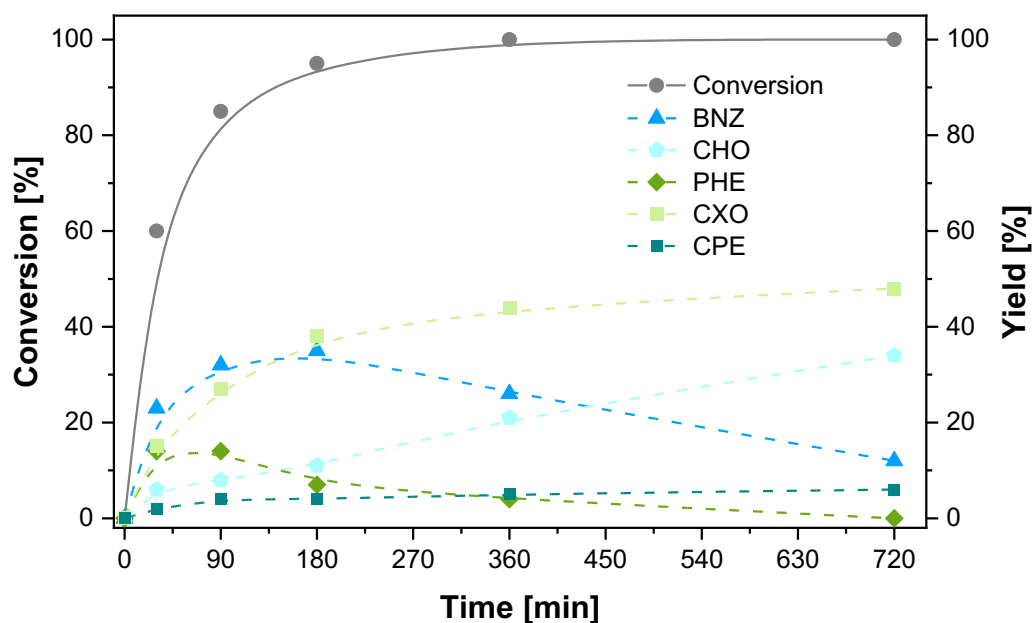
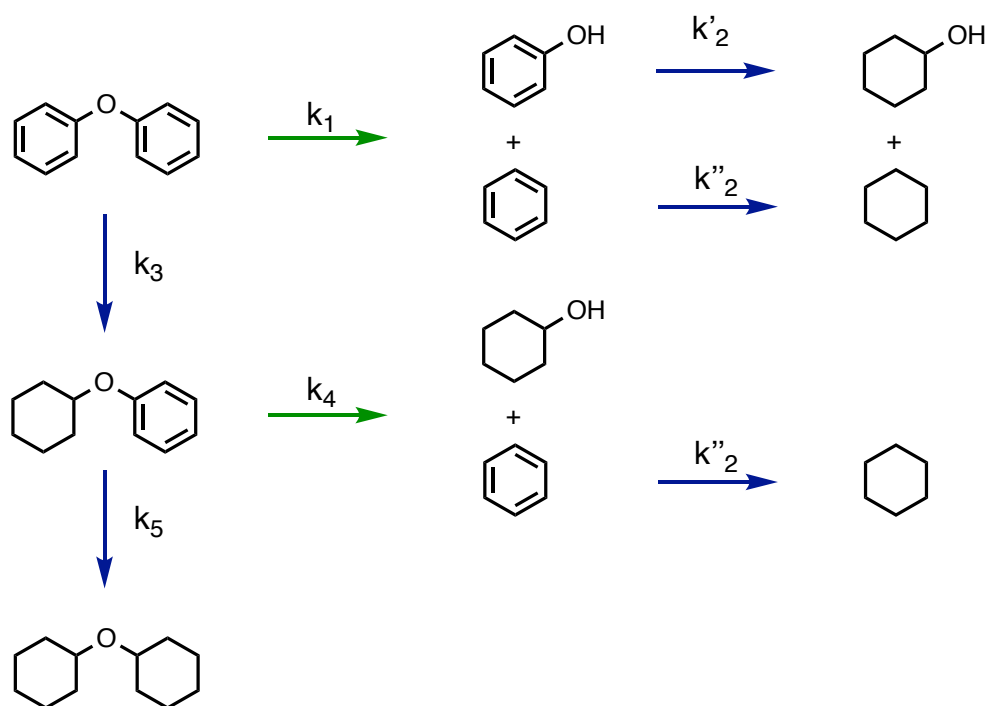


Fig. 2. Product yield in the conversion of DPE on using the Ru/C catalyst under CTH conditions at 210 °C against time (reaction conditions: 0.100 g of catalyst; 40 mL of DPE 0.1 M; N₂ pressure: 10 bar; stirring: 500 rpm).

The DPE conversion was completed after 6 h of reaction. As the reaction proceeds, benzene and phenol yields progressively increase on increasing reaction times, reaching the highest value at 180 min. Then, they progressively decrease because of further hydrogenation leading to cyclohexane and cyclohexanol respectively.

A simplified kinetic model of the CTH of DPE in the presence of 2-PrOH as solvent/H-donor was also developed (Scheme 2) assuming that all possible reactions of Route A and Route B are all of pseudo first order and irreversible (see supporting information for all details).



Scheme 3. Products and reaction kinetics constants in CTH of the DPE

The variation of the DPE concentration as a function of time is obtained by taking into account the reaction kinetics of DPE hydrogenolysis and hydrogenation, including the related kinetic constants k_1 and k_3 , respectively:

$$-\frac{d}{dt}[DPE] = k_1[DPE] + k_3[DPE] \quad (8.0)$$

By integration, it is possible to obtain the concentration of the DPE as:

$$[DPE] = [DPE]_0 \cdot e^{-K_{TOT}t} \quad (8.1)$$

where $[DPE]_0$, is the initial concentration and K_{TOT} , is given by k_1+k_3 .

Figure S1 shows the plot of the $[DPE]/[DPE]_0$, as a function of the reaction time. Experimental points were fitted by using eq. 8.1, describing the exponential decrease of the DPE concentration over time, using the kinetic constant $K_{TOT} = 0.031 \pm 0.003 \text{ min}^{-1}$ ($R^2 > 0.97$) (Tab. S1).

At any time of the reaction, the following stoichiometric condition must be satisfied (eq. 8.1):

$$[DPE]_0 = [DPE] + [PHE] + [BNZ] + [COH] + [CHX] + [CPE] + [DCE] + [OP] \quad (8.1)$$

The initial concentration of the DPE is given by the addition of concentrations of all the reaction products and the unreacted DPE. However, the experimental evidence indicates that contributions of the cyclohexyl phenyl ether (CPE), dicyclohexyl ether (DCE) and of other secondary products, can be reasonably neglected as their concentration are very small compared to the other products, throughout all reaction time. Therefore, eq. 5.4 can be simplified as:

$$[DPE]_0 \cong [DPE] + [PHE] + [BNZ] + [COH] + [CHX] \quad (8.2)$$

Thus, products deriving from DPE transformation are phenol, benzene, cyclohexane and cyclohexanol. Fig. S2 shows the variation of the products concentration normalized with respect to the initial concentration of DPE. The first two products, phenol and benzene, show the typical trend of reaction intermediates, whose concentration, described by equations 8.3 and 8.4 (see Supporting Information for the description of the kinetic model), increases rapidly over time until reaching a maximum, then decreases reaching an almost constant value, tending to zero very slowly (fig S2 black and red lines).

$$[PHE] = \frac{k_1 [DPE]_0}{k'_2 - k_1} \cdot (e^{-k_1 t} - e^{-k'_2 t}) \quad (8.3)$$

$$[BNZ] = \frac{k_1 \cdot [DPE]_0}{k''_2 - k_1} \cdot [e^{-k_1 t} - e^{-k''_2 t}] \quad (8.4)$$

where fitting values are $\overline{k_1} = 0.007 \pm 0.001 \text{ min}^{-1}$, $\overline{k'_2} = 0.019 \pm 0.001 \text{ min}^{-1}$, and $\overline{k''_2} = 0.006 \pm 0.001 \text{ min}^{-1}$

The kinetic of benzene is a little bit slower than that of phenol (after about 200 min from the beginning of the reaction with respect to 50 min for phenol). Cyclohexane and cyclohexanol, as final products, show a monotonous growing trend over time approaching a plateau value after a certain time. The initial rate of cyclohexanol production is faster than that of cyclohexane and the plateau value is

reached early with respect to cyclohexane (Fig. 1b), (after about 400 minutes). The integrated kinetic equations, describing the concentration of the above products, are:

$$[CHX] = \frac{k_2'' \cdot [DPE]_0}{k_2'' - K_{TOR}} \cdot (k_2'' - k_1 + k_1 \cdot e^{-k_2'' t} - k_2'' \cdot e^{-K_{TOR} t}) \quad (8.5)$$

$$[COH] = [DPE]_0 \left\{ 1 - e^{-K_{TOR} t} - \frac{k_1 [DPE]_0}{k_2' - k_1} \cdot (e^{-k_1 t} - e^{-k_2' t}) - \frac{k_1}{k_2'' - k_1} [e^{-k_1 t} - e^{-k_2'' t}] - \frac{k_2'' \cdot [DPE]_0}{k_2'' - K_{TOR}} \cdot (k_2'' - k_1 + k_1 \cdot e^{-k_2'' t} - k_2'' \cdot e^{-K_{TOR} t}) \right\} \quad (8.6)$$

3.4 Temperature effect and catalyst stability tests in the transfer hydrogenolysis reaction of DPE promoted by the Ru/C catalyst

On the basis of the obtained results, the Ru/C emerges as a more efficient catalyst than Pd/C for the C–O bond breaking of diphenyl ether in alcoholic solvents together with a less pronounced tendency towards the hydrogenation of the aromatic ring. Therefore, for all other experiments, Ru/C was chosen as the heterogeneous catalytic system to unravelling the reductive upgrading of biomass model aromatic ethers under CTH and **lignin-first** conditions.

Under CTH conditions, the reaction temperature was varied in the range of 120–240°C maintaining constant the reaction time of 180 min (Fig. 3). The DPE conversion increases almost linearly from 27, 45, 60 to 95% (120, 150, 180 to 210°C, respectively) on increasing the reaction temperature, reaching the total conversion at 240 °C. The selectivity, on the other hand, did not change significantly from 120 to 180°C with an increase of the production of cyclohexanol and cyclohexane at higher reaction temperatures, indicating that the hydrogenation of aromatic ring is favored in these conditions.

In any case, the highest yield of aromatic compounds was registered at 210 °C. In view of the above results, two key points can be stated: (i) 2-PrOH is a strong hydrogen donor also at low reaction temperatures and (ii) the presence of cyclohexane and cyclohexyl phenyl ether as reaction products, in

the temperature range investigated (even at 120°C), confirms the co-presence of the hydrogenation-hydrogenolysis pathway (Route B) in the DPE conversion under CTH conditions.

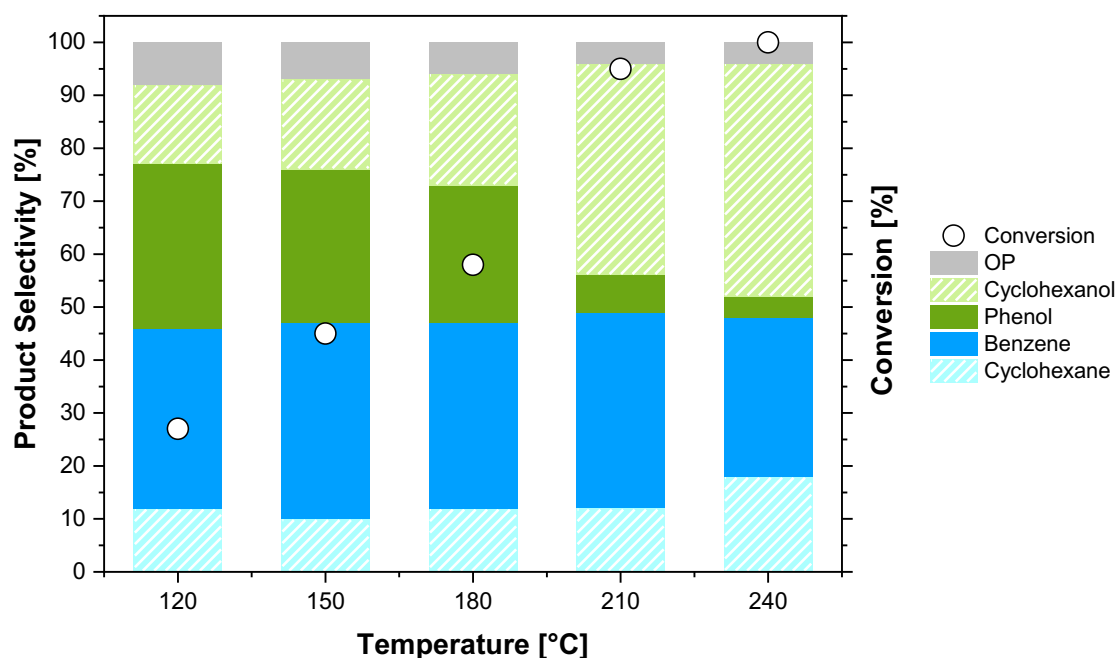


Fig. 3. Effect of reaction temperature on the DPE conversion and product selectivity with the Ru/C catalyst under transfer hydrogenolysis conditions at 210 °C (reaction conditions: 0.100 g of catalyst; 40 mL of DPE 0.1 M in 2-propanol; N₂ pressure: 10 bar; reaction time: 3 hours; stirring: 500 rpm).

Finally, Ru/C was also tested in consecutive recycling reactions to gather information on the catalyst reusability under the reaction condition adopted (210 °C for 3 h). Ru/C maintains its activity after five consecutive runs and no significant changes in DPE conversion was observed highlighting the good stability of the catalyst (Fig. 4.). Interestingly, a lower tendency in hydrogenating phenol and benzene is observed during recycling tests.

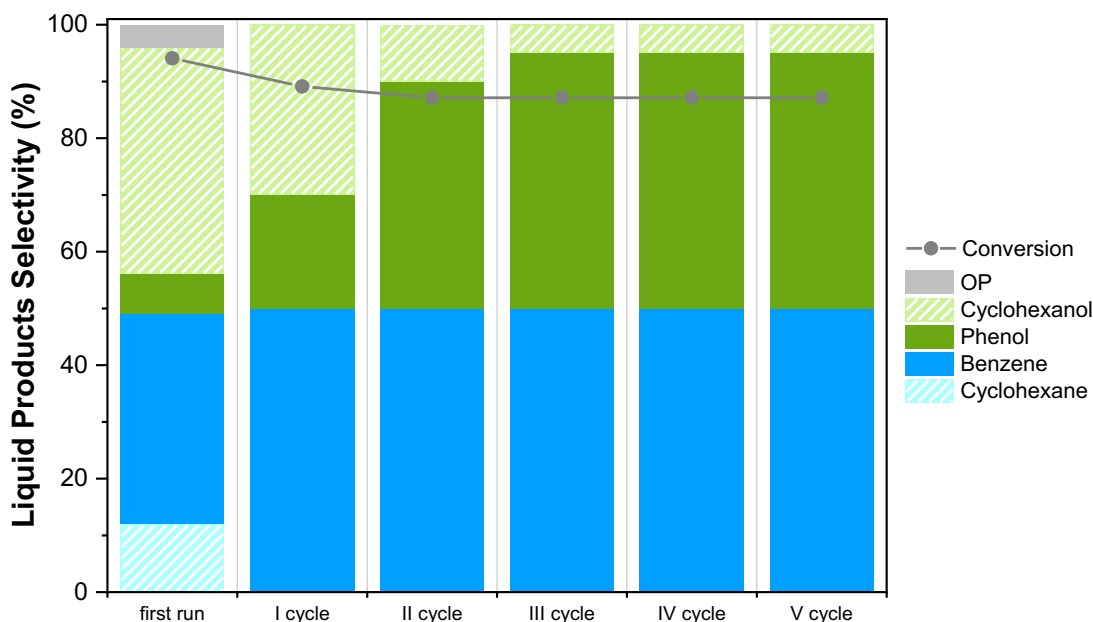


Fig. 4. Recycling tests for Ru/C catalyst in the CTH of DPE (reaction conditions: 0.100 g of catalyst; 40 mL solution of DPE 0.1 M in 2-propanol; temperature: 210 °C; time: 180 min; initial N₂ pressure: 10 bar; stirring: 500 rpm).

3.5 C-O bond cleavage of diphenyl ether under lignin-first conditions

With the optimized reaction conditions in hands, we then investigated the catalytic conversion of DPE under lignin-first conditions by using water as co-solvent in the reaction media (Fig. 5 and Table S.2).

No DPE conversion was observed in the reaction carried out in the presence of sole water as solvent as a consequence of the absence of any H-source in the reaction media. The cleavage of the etheric C-O bond increases by increasing the amount of isopropanol with a complete DPE conversion already reached with a composition of isopropanol/water ratio of 25/75 (v/v), being the same isopropanol/water ratio of 25/75 (v/v) the best composition in terms of aromatic compounds production.

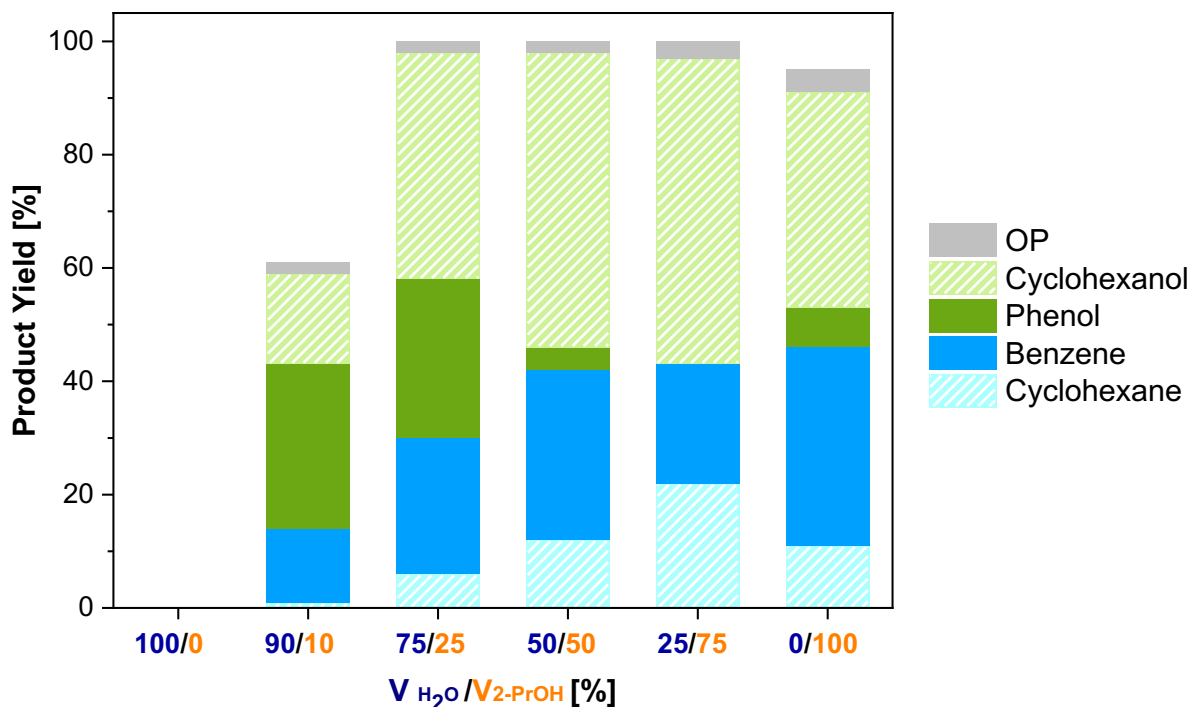


Fig. 5. Reductive upgrading of DPE under **lignin-first** conditions promoted by Ru/C catalyst (reaction conditions: 0.100 g of catalyst; 40 mL solution of DPE 0.1 M; temperature: 210 °C; time: 180 min; initial N₂ pressure: 10 bar; stirring: 500 rpm).

Remarkably, the yield and distribution of phenolic compounds (phenol and cyclohexanol) is deeply influenced by the presence of water in reaction media. Indeed, the percentage of hydrolysis increases from 11% to 50% upon using 2-PrOH/H₂O at 75/25 and 90/10 % as solvent mixture, respectively. At higher water concentrations, the amount of phenol and cyclohexanol increases clearly indicating the occurrence of the reductive hydrolysis reaction (Route C).

To verify that the formation of cyclohexanol arises mainly from the reductive hydrolysis route of DPE rather than from the hydrogenation+hydrolysis of CPE, cyclohexyl phenyl ether was subjected to the same “lignin-first” reaction conditions (0.100 g of catalyst; 40 mL 2-PrOH/H₂O at 75/25 solution of CPE 0.1 M; temperature: 210 °C; time: 180 min; initial N₂ pressure: 10 bar; stirring: 500 rpm). A very low conversions of CPE (5%) into CXO (100% selectivity) was obtained confirming that, under the reaction conditions employed, this reaction do not contribute significantly to the observed reductive hydrolysis of DPE. The preference for the hydrolysis route over the Ru/C catalyst in water was

confirmed by performing an analogous reaction in the presence of molecular H₂ (10 bar) where a 100% DPE conversion with an impressive selectivity of 65% to cyclohexanol was registered (Table 2).

Accordingly, by using H₂ as H-donor, a high DPE conversion can be achieved also in ethanol/water (100%) and methanol/water (85%) media. Also in these cases, a **concentration increase** of phenol-deriving compounds is registered. Noteworthy, diphenyl ether can be fully hydrogenated also into dicyclohexyl ether (10% selectivity) in the presence of methanol/water (25/75) as solvent and molecular hydrogen as H-donor source. As expected, analogous reactions performed in the absence of molecular hydrogen provided a conversion of DPE < 2% both in ethanol/water and in methanol/water, whereas, in presence of H₂ (10 bar) the relative conversions were 100% and 85%, respectively.

Table 2. Reductive upgrading of DPE promoted by Ru/C catalysts under **lignin-first** conditions (reaction conditions: 0.100 g of catalyst; 40 mL solution of DPE 0.1 M; temperature: 210 °C; time: 180 min; initial H₂ or N₂ pressure: 10 bar; stirring: 500 rpm).

Solvent	H-source	Conversion [%]	Liquid Product Selectivity [%]						
			BEN	CHO	PHE	CXO	CON	CPE	DCE
H ₂ O/2-PrOH (75/25)	H ₂	100	-	35	-	65	-	-	-
H ₂ O/2-PrOH (75/25)	2-PrOH	100	24	6	28	40	1	1	-
H ₂ O/EtOH (75/25)	H ₂	100	4	25	7	56	-	4	4
H ₂ O/EtOH (75/25)	EtOH	< 2	-	-	-	-	-	-	-
H ₂ O/MeOH (75/25)	H ₂	85	-	27	-	60	-	3	10
H ₂ O/MeOH (75/25)	MeOH	< 2	-	-	-	-	-	-	-

BEN: benzene; CHO: cyclohexane; PHE: phenol; CXO: cyclohexanol; CON: cyclohexanone; CPE: cyclohexyl phenyl ether; DCE: dicyclohexyl ether.

3.6 Reductive upgrading of benzyl-phenyl ether (BPE) and phenethyl phenyl ether (PPE) under **lignin-first** conditions.

Finally, in order to extend the substrate scope, the hydrogenolysis of benzyl-phenyl ether (BPE) and phenethyl phenyl ether (PPE) was investigated in absence of added hydrogen (Fig. 5).

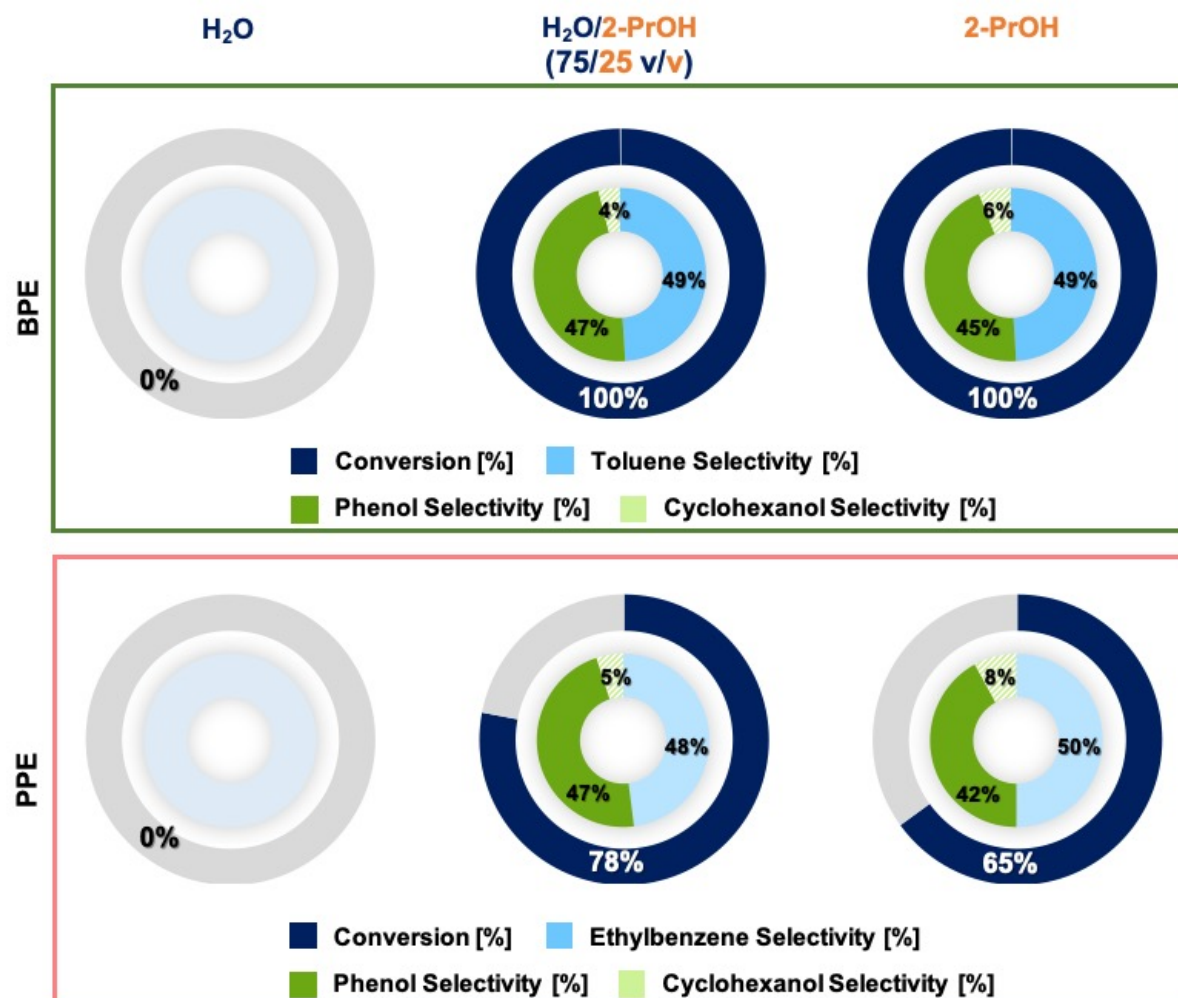


Fig. 5. Reductive upgrading of BPE and PPE under **lignin-first** conditions in absence of added hydrogen promoted by Ru/C catalyst (reaction conditions: 0.100 g of catalyst; 40 mL solution of DPE 0.1 M; temperature: 210 °C; time: 180 min; initial N₂ pressure: 10 bar; stirring: 500 rpm).

A higher BPE conversion, with respect to DPE, can be easily obtained in the presence of 2-propanol as H-donor because of the lower dissociation energies of the C–O bonds involved.

Most important, experimental data demonstrate that, in contrast with DPE, the hydrogenolysis of BPE and PPE has a higher selectivity towards aromatic products. This indicates that the hydrogenolysis of the etheric C–O bond in BPE and PPE generally precedes the hydrogenation (Route A). The aromatic ring hydrogenation is very little pronounced in agreement with a recent report where it was

demonstrated that the hydrogenation process of phenol – under CTH conditions - is very sensitive to the co-presence of other aromatic species on the reaction system with a decrease of the aromatic ring saturation that follows the order phenol + benzene > phenol + toluene > phenol + ethylbenzene [52].

Surprisingly, reactions carried out in the presence of water as co-solvent provide an almost equimolar mixture of phenol + toluene (in the case of BPE) and phenol + ethyl benzene (in the case of PPE) derivatives that can be surely attributed to the unique presence of hydrogenolysis-hydrogenation pathway (Route A). The suppression of the reductive-hydrolysis route could stem from the higher steric hindrance of both BPE and PPE with respect to DPE that lowers the adsorption of their aromatic rings onto the Ru metal surface thus limiting the hydrogenation process. Thus, the lower tendency to undergo a hydrogenation process - in absence of a readily available H-donor source - is more pronounced for phenethyl phenyl ether that shows a lower conversion with respect to DPE and BPE.

4. Conclusions

The catalytic conversion of diphenyl ether (DPE), phenethyl phenyl ether (PPE) and benzyl-phenyl ether (BPE) has been investigated in the presence of Ru/C and Pd/C under **lignin-first** conditions by using C1-C3 alcoholic H-donor/solvents (methanol, ethanol and 2-propanol), used as such or in mixture with water both in the presence and in the absence of molecular H₂.

Ru/C was found to be a better catalytic system, with respect to Pd/C, in the production of aromatic compounds from lignin model diphenyl ether (DPE) that was studied as model molecule to investigate the complex hydrogenolysis-hydrogenation-hydrolysis reactions that occur in the cleavage of the etheric 4-O-5 C-O bond.

The direct C-O bond breaking (hydrogenolysis-hydrogenation route) is preferred in the presence of 2-propanol (that provides best results both in terms of DPE conversion as well as in the production of aromatic compounds), whereas the hydrogenation-hydrogenolysis pathway is favored by using molecular hydrogen. At the same time, by adding water as co-solvent, the impact of the reductive hydrolysis-hydrogenation route becomes more significant allowing the preferential formation of hydrogenated phenolic compounds.

Noteworthy, a very high selectivity to the hydrogenolysis was observed in the case BPE and PPE as a consequence of both their higher steric hindrance, with respect to DPE, that limits the adsorption of their aromatic rings onto the Ru metal surface as well as to the lower tendency of phenol to undergo a hydrogenation process when toluene or ethyl benzene are present in the reaction medium.

Credit authorship contribution statement

E. Paone: Conceptualization, Supervision, Methodology, Investigation, Writing - original draft. **A. Beneduci:** Conceptualization, Methodology, Investigation. **G. A. Corrente:** Methodology, Investigation, Writing - original draft. **A. Malara:** Methodology, Investigation. **F. Mauriello:** Conceptualization, Supervision, Writing - review & editing, Funding acquisition.

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