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**Transfer hydrogenolysis of lignin and its
derived aromatic ethers promoted by
heterogeneous bimetallic Pd-based catalysts**

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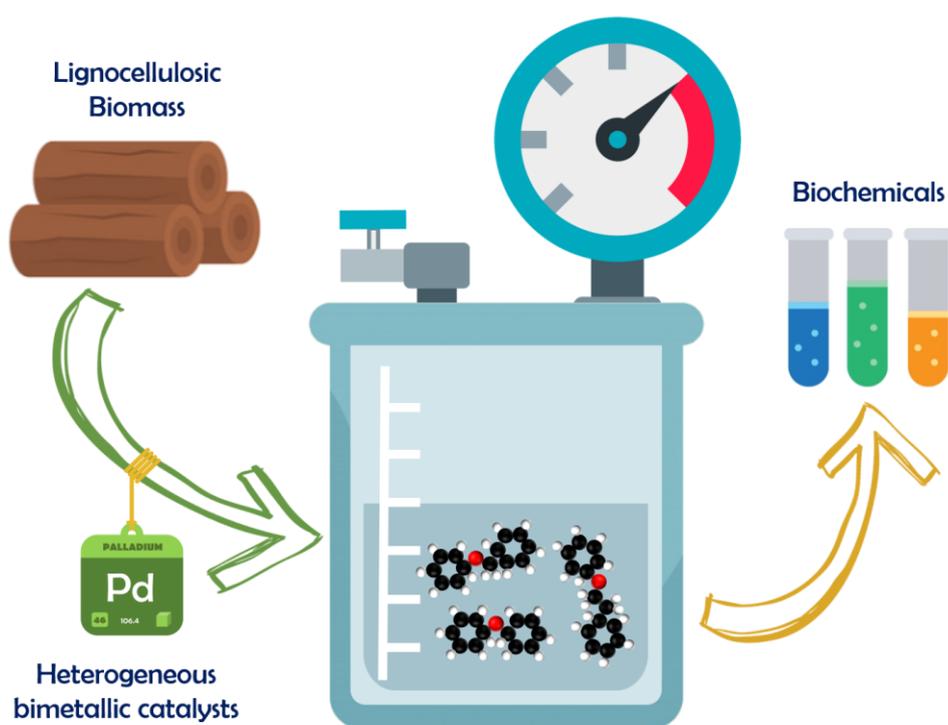
Abstract

This doctoral work is focused on the sustainable valorization of lignin and its derived molecules, through the application of the transfer hydrogenolysis technology, by using heterogeneous Pd-based catalysts, in order to achieve products with high-added value. In particular, the thesis, based on hydrogenolysis processes study, starts with three model molecules of lignin: Benzyl Phenyl Ether (BPE), Phenethyl Phenyl Ether (PPE) and Diphenyl Ether (DPE) that mimic typical C-O lignin linkages, such as α -O-4, β -O-4, and 4-O-5 bonds.

The work uses heterogeneous bimetallic coprecipitated Pd-based catalysts (Pd-M catalysts), such as Pd/Fe₃O₄, Pd/Co and Pd/Ni, and their textural and structural properties have been deeply elucidated through several characterization techniques (XRD, TEM, SEM, H₂-TPR, XPS and EXAFS) in order to highlight the key factors that influence the catalytic results observed. A comparison of the performance of bimetallic Pd-M catalysts used and that of the commercial Pd/C is also included.

The last part of the thesis is dedicated to the investigation of the transfer hydrogenolysis reaction of lignin, obtained by the organosolv process.

GRAPHICAL ABSTRACT



Graphic representation of the research activities dealing with the PhD thesis “Transfer hydrogenolysis of lignin and its derived aromatic ethers promoted by heterogeneous bimetallic Pd-based catalysts”.

1

Introduction

1.1 Sustainable chemicals production from lignocellulosic biomasses

For millennia, the human economy has been based almost exclusively on agricultural resources and, only in the last two centuries, the main source of energy at man's disposal has become that of fossil origin: first coal and then petroleum and natural gas.

Petrol oil and its derivatives are everywhere around us: on the road asphalt, in domestic detergents, in our films, in our records, clothes, cars, becoming the reason of serious problems, including international wars and tensions.

Although it is often renamed as "black gold" for its importance and preciousness, petroleum creates a series of drawbacks, among which, one of the most important is certainly pollution. It is known, in fact, how emissions, produced by the combustion of fossil fuels are the main cause of environmental problems, such as the greenhouse effect (in the case of carbon dioxide) and acid rain (in the case of sulfur oxides and nitric oxides).

So, in recent years, the increasing use of raw oil, the awareness of environmental problems and the concerns about the depletion of fossil energy resources have brought human societies to reinforce the need at alternative energy

sources possibly biodegradable and renewable, which would allow local resources to be used in a sustainable way.

There are several alternatives that can meet sustainability criteria, such as solar, wind, geothermal energies and appropriate biomasses. The biomasses, produced and used in a cyclical way, constitute a renewable and environmentally friendly energy resource.

So, biofuels and agricultural resources, used in the past and then supplanted by fossil fuels, due to their lower production costs, have recently been "dusted off" and changes in consumer attitudes towards "green" products [1] as well as government initiatives for sustainable development programs and regulations are surely the key driving factors for the development of the bio-based chemical industries and refineries [2-6].

While many criticisms have been raised towards the first generation bio-energies and biofuels since they were in direct competition with the human and animal food reducing, at the same time, the land availability [7], we have recently got a significant progress in the production of building block and chemical intermediates from lignocellulosic wastes and residues [8-16]. This because their use in chemical industry presents several advantages including: (i) less toxic by-products and lower environmental risks; (ii) the reduction of CO₂ emissions; (iii) a minor dependence on fossil resources and/or foreign commodities; (iv) the use of indigenous raw materials that can add value in many agriculture products or processes.

Three different approaches have been, so far, used for biobased refineries: (i) the production of an identical petrochemical building block starting from lignocellulosic

platform molecules; (ii) the use of platform molecules to produce the first petrochemical intermediates; (iii) the synthesis of new products alternative to the petrochemical ones starting from the platform molecules and/or their intermediates. It is expected that the market relative to all bio-based chemicals and materials will increase at an annual growth rate of 16.53% in the forecast period 2018-2026 [17] with a total product value of about 103 billion of euros by 2050 [18].

To replace fossil-derived fuels and chemicals, resources must be renewable, of sufficient abundance and not in competition with agricultural land and food production. In this context, the lignocellulosic biomasses (abundant and inedible resources that can be easily obtainable also from agricultural residues and waste materials) are placed in a great position to compete with fossil fuels. Furthermore, they have become one of the most eco-attractive, environmentally friendly and alternative candidates to replace non-renewable petroleum-based resources and their use has matured consciously, becoming one of the most promising solutions in modern industrial chemistry.

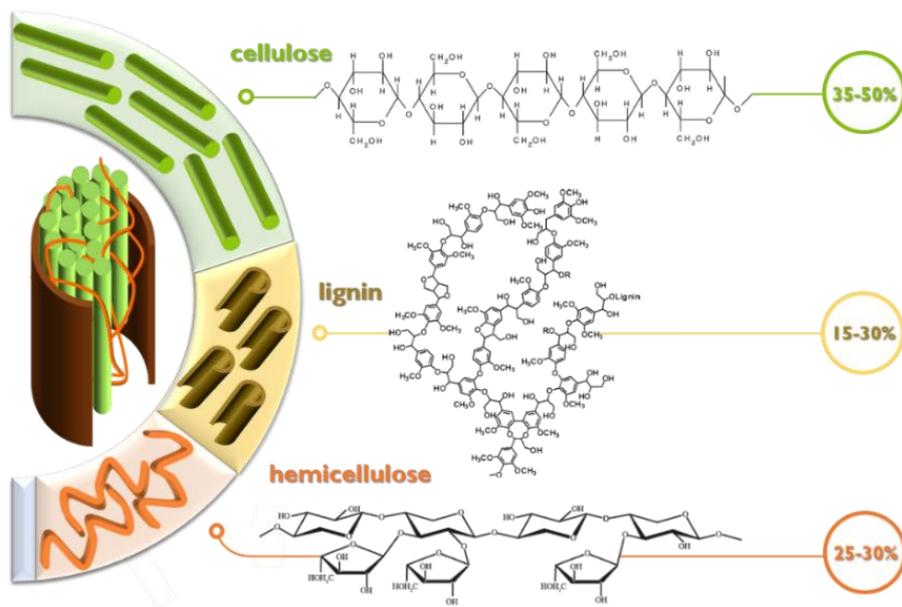


Figure 1.1 Chemical structure of the lignocellulosic material and its constituents: cellulose, hemicellulose, lignin [14].

Since lignocellulosic biomasses have a complex “chemical-architecture”, they can be valorized through a variety of chemical routes and industrial processes [10-19]. One strategy implies a first deconstruction into its three main components: cellulose (35–50%), hemicellulose (25–30%) and lignin (15–30%) (Figure 1.1).

Thus, the three main constituents of lignocellulosics can be transformed into biomass-derived platform chemicals with varying compositions and functionalities. A non-exhaustive representation of the most important lignocellulosic-derived molecules for chemical industry are reported in Figure 1.2.

Cellulose, the largest single component of lignocellulosic biomasses, is a polymer characterized by glucosidic units, with an average molecular weight of around 100.000, bonded through β -glycosidic linkage at the positions 1 and 4 [19].

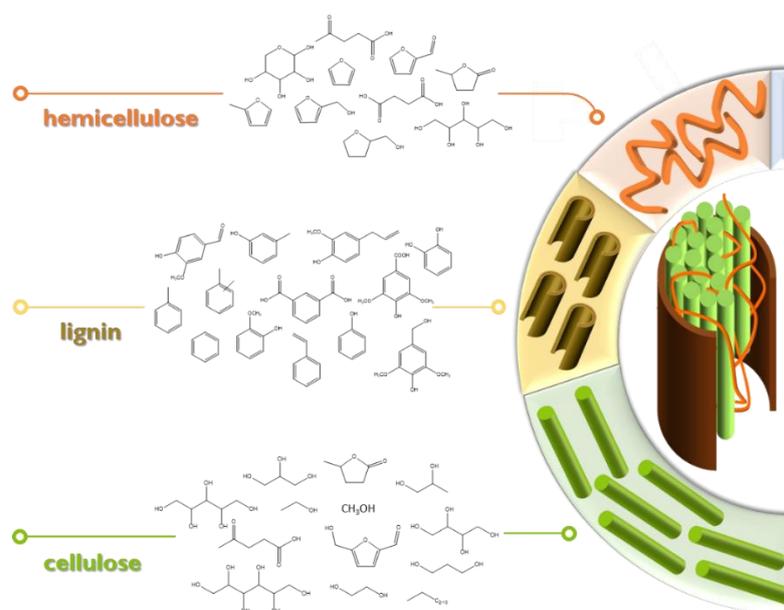


Figure 1.2 Cellulose, hemicellulose, lignin derived molecules.

The β -1,4-glycosidic linkages leads to side-by-side disposition of the pyranose rings in long chains, forming an intense intramolecular hydrogen bonding between groups staying nearby the glycosidic bond; this feature maintains the structure of cellulose as a “planar sheet”, which can be packed as well through hydrogen bonds and a large number of Van der Waals weak interactions. In this arrangement, most chemical functions of cellulose are not accessible to enzymes, chemicals and solvents. Cellulose is not digestible by humans, making its utilization in the chemical manufacture irrelevant for the human food supply. Therefore, the conversion of cellulose into added-value chemicals and/or fuel components is one of the core technologies in the modern bio-refinery [20-21]. The first step, for cellulose valorization, is based on its depolymerisation into oligomers and glucose followed by several type of catalytic reactions (hydrogenation, oxidations, esterification, etc.) for the

manufacture of a pool of chemicals such as C₆–C₂ polyols, levulinic acid, hydroxymethylfurfural (HMF), among others [20-24]. Polyols, with their peculiar chemical properties, represent an important resource for production of several building-block chemicals. Indeed, sorbitol (C₆ polyol), xylitol (C₅ polyol) and glycerol (C₃ polyol) are included in the list of the most important 12 potential biomass-derived platform chemicals [25]. Moreover, among the family of biomass derived polyols, glycerol (C₃ polyol) has become a primary building block being the main by-product in the biodiesel production [26-34].

Hemicellulose, unlike cellulose, has a heterogeneous chemical structure of pentoses, hexoses and sugar acids. Hardwood hemicelluloses is chiefly composed by xylans whereas softwood hemicellulose mainly consists of glucomannans [35-36]. The chemical hydrolysis of hemicelluloses into xylose and arabinose is generally afforded in high yields and low costs. Xylose, in particular, is largely used in modern biorefineries to produce furfural (2-furaldehyde) through several homogeneous and heterogeneous catalytic processes [37]. Furfural, with a world production of about 200,000 tonnes per year, is the key precursor of important building blocks such as furfuryl alcohol, 2-methylfuran, 2-methyltetrahydrofuran and levulinic acid [38-40].

Lignin is unique among other biomass components, being characterized by an aromatic sub-structure with a large amount of etheric C–O bonds (Figure 1.3).

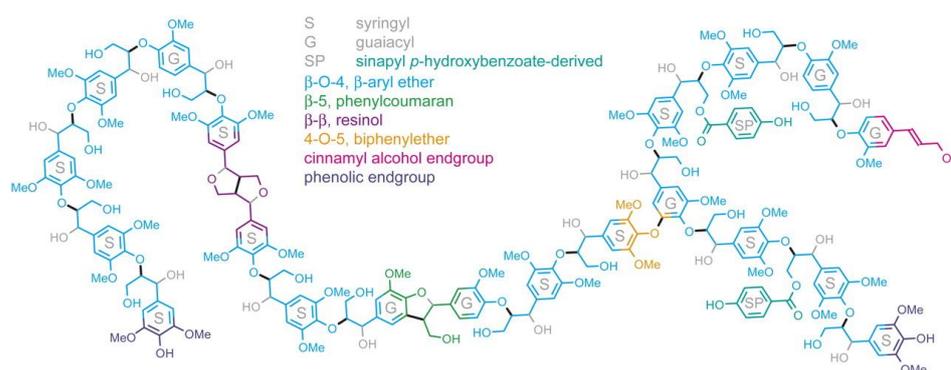


Figure 1.3 Chemical structures of lignin polymer and structures of its chemical linkages.

Lignin has a complex and variable structure derived from the polymerization of three monolignols: synapyl, coumaryl, coniferyl alcohols also called monolignols, whose proportions depend on the different kind of plant species [41].

The native constituents of lignin are therefore of particular interest for a lignocellulosic biorefinery aimed to the sustainable production of green aromatic compounds. At present, industrial processes are limited to vanillin and “kraft lignin” (about 60 kt/year) manufacture but the research on the sustainable production of chemicals from lignin has developed rapidly in the last years [42-46]. To this regard, one of the major challenges is the low cost-effective catalytic depolymerization of lignin preserving its aromatic nature [47-60]. The efficient cleavage of the oxygen bridged linkages is a key step for the valorisation of lignin and its derived compounds. Although, this process is difficult due to the high strength and stability of the etheric C-O bonds [61].

Only less than 2% of the 1.5–1.8 billion tons of industrial lignin waste are used in the world annually. Most of the lignin waste are dumped or burned as low-grade fuel, which not only causes wastage of resources, but also gives

serious environmental pollution. Therefore, it is imperative to promote lignin valorization through technological advancement for the realization of sustainable resource management. By means of tailored thermochemical technologies of lignin, a range of value-added chemicals can be produced such as ethyl benzene (important intermediate for organic synthesis), guaiacol (phenolic resin making), phydroxyl acetophenone (cholagogue drug making and perfume synthesis), vanillin (important perfume and pharmaceutical intermediate), and carbon materials (supercapacitors and catalysts). Phenols are widely used in household products and as intermediates for industrial synthesis. Phenol itself is used (in low concentrations) as a disinfectant in household cleaners and in mouthwash, while cyclohexanol is an important feedstock in the industrial chemistry being used as a precursor to nylons, plastics, detergents and insecticides.

1.2 Lignin extraction technologies

The successful valorization of lignin to high value-added chemicals is mainly determined by an interplay of three important biorefinery procedures: (i) lignocellulose fractionation (Figure 1.4), (ii) lignin depolymerization (Figure 1.5), and finally (iii) upgrading towards desired chemicals [62].

The various fractionation technologies are divided into two distinct classes.

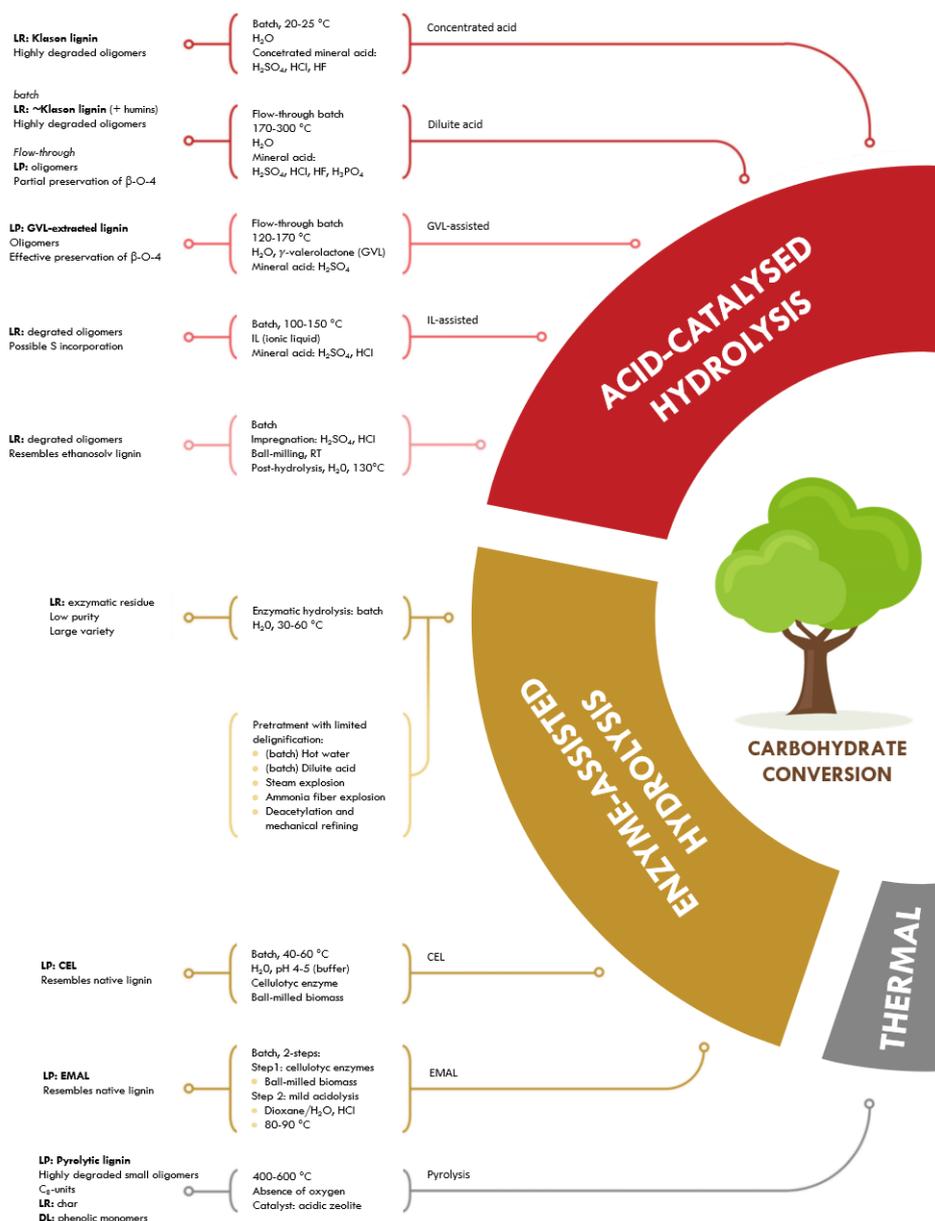


Figure 1.4 Biomass fractionation methods *via* carbohydrate conversion (modified from Ref. [62]).

The first class covers methods that focus on the liberation of lignin from the biomass matrix (i.e. delignification), while the (hemi)cellulose carbohydrates are preserved in the form of a delignified pulp. Depending on the method used, the lignin is isolated as a solid lignin precipitate (LP) or as a depolymerised lignin oil (DL).

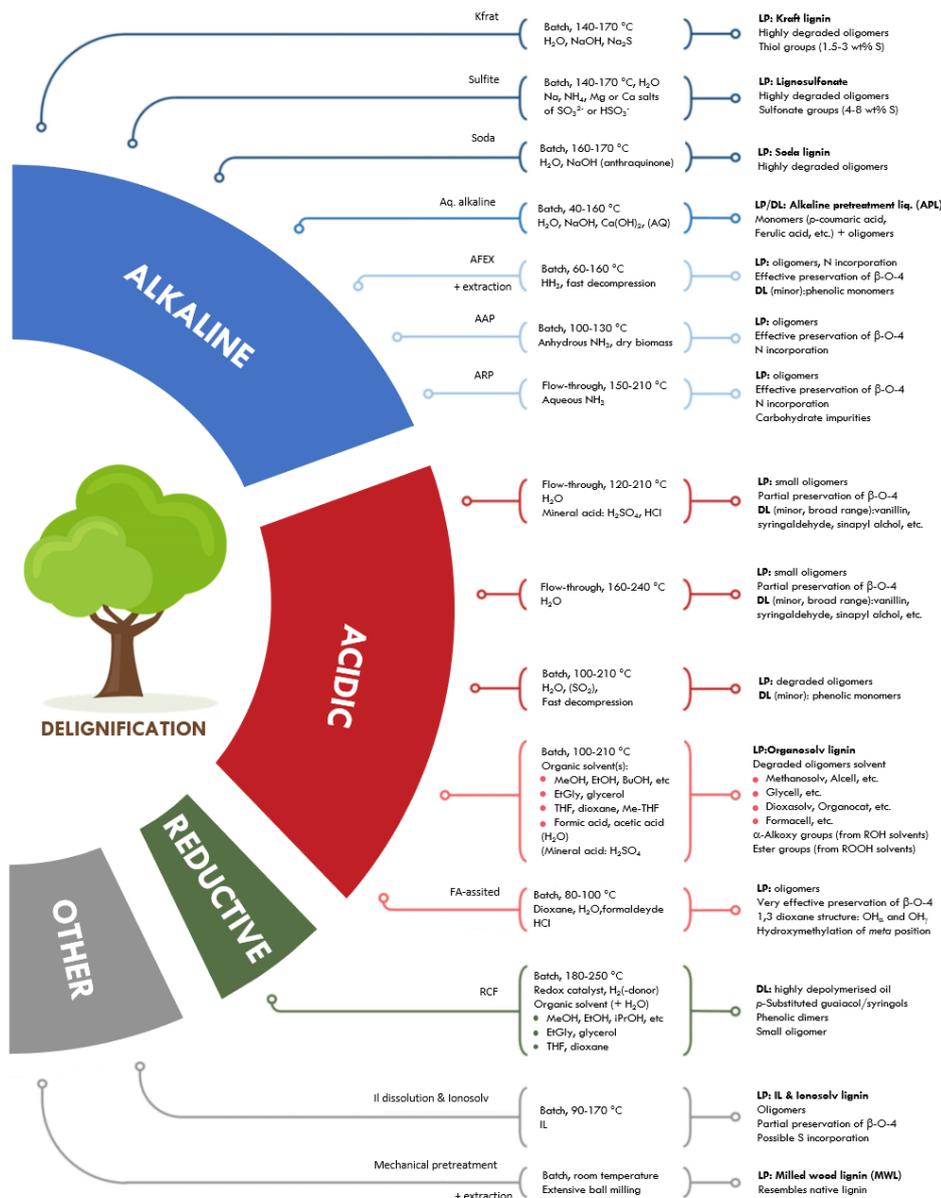


Figure 1.5 Biomass fractionation methods *via* delignification processes (modified from Ref. [62]).

The second class of lignocellulose fractionation strategies includes methods that target the conversion and solubilisation of the carbohydrate fractions. Herein, lignin is mostly isolated in the form of an insoluble lignin residue (LR) or as a lignin precipitate (LP).

Surely the chemistry of lignin radically depends on the extraction process employed and is not related to the native

botany [63]. Among all possible fractionalization technologies, pulping processes are surely among the most adopted and can be classified into two main categories (sulfur processes and sulfur-free processes [64]).

The lignin obtained from sulfur-free processes generally has a low molecular weight and its structure is much closer to the natural lignin compared to those coming from the other processes. Due to its characteristics, it is an interesting source of aromatic and low molecular weight phenolic compounds.

Kraft pulping (sulfur pulping process)

Kraft pulping is the main pulping process, producing over 90% of all chemical pulps. The term "kraft" comes from the German language and means "strong". During the kraft pulping, wood is processed in an aqueous alkaline solution (pH = 13) of NaOH and Na₂S, termed white liquor. The polymer molecules of lignin break thanks to the action of hydrosulfide ions (HS⁻) and dissolve in a black liquid, termed black liquor, to be then recovered by drying [21,82,83,89]. Kraft lignin, is highly condensed and contains a low amount of residual β-O-4 bonds [65-68]. Furthermore, it also incorporates sulfur in the form of thiol groups [65] which can complicate the downstream valorisation (e.g.catalyst poisoning)[69].

Sulfite pulping (sulfur pulping process)

Sulfite pulping is the second most important chemical pulping process, but its market share has decreased drastically with the rise of the more versatile and efficient kraft process [70,71].

The biomass is treated with sulfite salts (SO₃²⁻) or bisulphites (HSO₃⁻) having as counterions, generally sodium

(Na⁺), calcium (Ca²⁺), potassium (K⁺), magnesium (Mg²⁺) or ammonium (NH₄⁺)(the pH is usually between 1.5 and 5, depending on the salt used).

The major reactions involved are hydrolysis, condensation and sulphonation. The dissolution of lignin in water is caused by the introduction of sulphite groups in the α position with respect to the alkyl chain. In addition, in order to be water-soluble, this type of lignin has an average value of molecular weight higher than that of lignin Kraft (15000-50 000 against 1000- 3000 Da) and a higher polydispersity index (6-8 against 2.5-3.5) [72].

Lignosulfonates are typically highly degraded (i.e. they contain newly formed C-C linkages and a decreased β -O-4 content) and have a higher sulfur content (4-8 wt%) compared to the lignin derived from the kraft procedure lignin [65, 71, 73, 74].

Organosolv pulping (sulfur-free pulping processes)

Organosolv pulping is a process in which biomass is treated with an organic solvent, often in combination with mineral acids and/or water[75-78]. Organosolv lignins are generally the purest lignins [72], since they contain many ramifications with a large number of active sites useful for subsequent chemical reactions. After the pulping process, lignin can be separated from the co-extracted hemicellulose fraction by precipitation from the pulping liquor, yielding organosolv lignin. Organosolv pulping thus enables the efficient fractionation of lignocellulose in its three major constituents: a solid cellulose pulp, a lignin precipitate, and an aqueous hemicellulose-derived stream [77]. Various solvents can be used, including alcohols (methanol, ethanol, butanol) [79-87] polyols (ethylene glycol, glycerol)[88-91]

cyclic ethers (THF, dioxane)[92-94] organic acids (formic acid, acetic acid) and ketones (acetone) [95-98].

A significant feature of organosolv pulping with concentrated alcohols is the incorporation of solvent-derived alkoxy groups at the α -position of lignin's alkyl chains and so alkoxylation protects the β -O-4 structure from undergoing degradation and condensation reactions.

The main properties of these lignins are the good solubility in organic solvents and the bad solubility in water. Other important characteristics are the high degree of purity and the low molecular weight. Furthermore, the continuous recycling of the used solvents allows to reduce the waste.

Soda pulping (sulfur-free pulping process)

Soda pulping is another traditional pulping process. It is related to Kraft pulping, with the major difference that soda pulping does not include the presence of Na_2S . The process is, therefore, characterized by the total absence of sulfur.

NaOH is used to dissolve the lignin that is obtained with a composition, compared to that obtained with the sulfur process, much more similar to the natural one. This feature makes the material very biocompatible and, as such, usable in areas such as animal nutrition. Furthermore, it has a lower lignin content, a more open structure, and a larger portion of alkalilable ester linkages, it is typically characterised by a low β -O-4 content [66, 68, 99] and can be isolated through precipitation.

The soda processes, which are not widespread in industry, are mainly applied to annual plants such as flax, bagasse and, sometimes, angiosperms.

1.3 Deoxygenative technologies: Hydrogenolysis and Catalytic Transfer Hydrogenolysis (CTH)

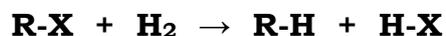
Hydrogenolysis processes, among several technologies, have gained a lot of attention since they allow the breaking of carbon-carbon and/or carbon-oxygen bonds in the presence of a hydrogen source [100-102]. One of the main drawbacks in hydrogenolysis, also known as “hydrodeoxygenation” if referred to the C–O bond breaking, is concerning the hydrogen management due to the poor solubility of molecular H₂ that leads to a considerable safety hazard due to the high pressure to be used. Moreover, hydrogen supply and related purchase, transport and storage costs need also to be considered.

The term hydrogenolysis, indeed, can be used in several contexts, such as the removal of various heteroatoms in hydrodesulfurizing or hydrotreating processes, also in combination with oxygen removal by hydrodeoxygenation. Therefore it needs some clarification on its definition [103].

Historically, the term hydrogenolysis goes back to Carleton Ellis, who described the hydrogenolysis of carbon-carbon bonds in organic substances, [104] although Sabatier and Murat had already described the hydrogenolysis of benzyl alcohol to toluene in 1915, [105] and Padoa and Ponti reported the hydrogenolysis of furfuryl alcohol as early as 1906 [106].

In terms of an exact definition, hydrogenolysis describes a chemical reaction whereby carbon-carbon or carbon-heteroatom single bonds are cleaved or undergo “lysis” by hydrogen [107].

The definition does not imply any mechanistic consideration, but refers to the stoichiometry of the reaction, which may be summarized as



where X can represent an alkyl chain or other functional groups containing heteroatoms (OH, OR, SH, NH₂, NR, etc.) [103].

Therefore, hydrogenolysis is a very well know reaction that has been efficiently adopted for the reduction of the oxygen content in lignocellulosic components and in their derived chemical platforms [108].

Generally, hydrogenolysis reactions are widely used in petroleum refineries, wherein sulfur, nitrogen, and oxygen heteroatoms are removed from hydrocarbon feedstocks, or more appropriately, the classic hydrogenolysis describes a type of reaction in which the monofunctional C-C bond cleavage occurs through addition of hydrogen over hydrogenation catalysts (Pt, Pd, Ni, metal oxides, or sulfides) occurs [103].

Alternatively to classic hydrogenolysis processes, which generally require high pressure of molecular hydrogen, catalytic transfer hydrogenolysis (CTH) reactions by means of simple alcohols (2-propanol, methanol and ethanol) and other H-donor molecules (hydrazine, tetralin, formic acid, cyclohexene, etc.) have been generally proposed as an efficient green alternative to the direct use of H₂ in the course of the last decade [109-111]. Since their introduction in 1903 when Knoevenagel revealed the disproportionation of dimethyl-1,4-dihydroterephthalate promoted by palladium black catalysts [112], CTH reactions are getting increasing attention improving the sustainability and economics of

hydrogenation reactions in modern green chemistry since: (i) they do not require hazardous pressurized molecular hydrogen; (ii) the hydrogen donors are generally readily available, inexpensive, obtainable from renewable resources and easy to handle and (iii) they generally produce valuable by-products (i.e., oxidized alcohol products). Moreover, CTH has been successfully adopted in reducing the oxygen content in biomass-derived feedstocks [111].

The ability of alcohols as potential source of hydrogen in CTH reactions can be correlated with their reduction potentials (defined as the difference of the standard molar free energy of formation between the alcohol and the corresponding carbonyl compound). Donor molecules used also as solvent reduces the safety problems of handling high-pressure and explosive hydrogen gas, reducing, at the same time, costs and complexity of bio-based industrial chemical plants. Moreover, at present, many H-donor molecules can be easily produced from renewable feedstocks [113]. Nonetheless of importance, H-donor molecules, due to their lower hydrogenation ability with respect to molecular H₂, generally allow a higher production of aromatic compounds.

1.4 Valorization of lignin and its derived aromatic ethers through hydrogenolytic technologies

Heterogeneous catalysts are the most widely used for lignin hydrogenolysis. The first study was reported by Harris et al. in 1938 [114] using solid Cu-CrO as catalyst. Since then, many more advances towards catalytic hydrogenolysis of lignin have been achieved.

In Table 1.1 results on the catalytic depolymerization of different types of lignin in presence of molecular H₂ are summarized.

Due to the complexity of the feedstock (lignin or wood), to be used, after depolymerization, reaction products include a mixture of oligomers or monomers. Furthermore, generally, harsh conditions (temperatures up to 300 °C and high initial H₂ pressures) and non-environmentally friendly solvents are adopted in order to perform hydrogenation/hydrogenolysis processes. In general, the hydrogenolysis is carried out using noble-metal based catalysts, such as ruthenium, platinum, palladium or rhodium.

The C–C bond dissociation energy in the linkages of lignin is as high as 384 kJ/mol, so devising a strategy to selectively cleave the C–O bond (bond dissociation energy: 218–314 kJ/mol) can be a more efficient aim. In order to achieve this goal, a lot of research has been directed in the cleavage of the C–O bond in aromatic ethers.

Nickel based catalysts have, so far, shown an excellent catalytic activity for the hydrogenolysis of lignin derived aromatic ethers with high stability and reusability. For this reason and for the good availability and the competitive market price of nickel precursors with respect to other transition metals, a remarkable development of heterogeneous Ni-based catalysts for the hydrogenolysis of aromatic ethers was reported in the last decades [126-130].

Among many, it is worth to underline some important contributions. The Hartwig group, developed highly selective heterogeneous nickel catalysts for the hydrogenolysis of diaryl, benzyl-aryl, and benzyl-alkyl ethers to form arenes and alcohols as exclusive products.

Table 1.1.1. Heterogeneous catalytic hydrogenolysis of lignin

Lignin type	Catalyst	Temperature [°C]	H₂ Pressure [bar]	Main products	Ref
Organosolv	CoOMoO ₃ /g-Al ₂ O ₃	400-450	70 o flow	THF-soluble products	[115]
Organosolv	Cu-CrO	260	223	Propylcyclohexanols	[115]
Organosolv	Ni-W/SiO ₂ -Al ₂ O ₃	370-410	10	THF-soluble products	[116]
Maple wood meal	NaOH + Raney Ni	173	138	Methoxyphenols	[117]
Spruce wood	Raney Ni	195	34	Methoxyphenols	[118]
Hardwood	WC	130-190	10-140	Oligomers	[119]
Organosolv	Raney Ni	300	70	Low-molecular fragments	[120]
Organosolv	Pt/C	175	50	Ethanol-soluble products	[121]
Lignosulfonate	Ni/AC	200-240	50	Lignin monomers	[122]
Woody biomass	Ni-W ₂ C	235	60	Lignin monomers	[123]
Klason	Pd/C	200	40	4-n-propanolsyringol	[124]
Poplar sawdust	Pd/C-H ₃ PO ₄	200	20	Monomeric phenols	[125]

Lercher/Zhao and co-worker deeply investigated the conversion of aromatic ethers in aqueous phase elucidating kinetics and reaction pathways over several supported Ni catalysts showing that the C-O bond is cleaved via parallel hydrogenolysis, hydrolysis and their integrated steps. In general, the C_{Alkyl}-O bond is selectively cleaved in presence of heterogeneous Ni catalysts, however the fast phenol hydrogenation is always observed. At the same time, Esposito et al. reported the hydrogenolysis of α -O-4, β -O-4, and 4-O-5 model compounds in ethanol at 100–150 °C (12 bar of hydrogen) using a novel Ni/TiN catalyst. High selectivity to aromatic compounds was observed for α -O-4 and β -O-4 models. Diphenyl ether (4-O-5 model), however, was also hydrogenated to cyclohexanol (49%). Strong Ni-TiN interactions were proposed to explain both the high activity and the good selectivity of the catalyst.

Other metal-based catalysts were less investigated. Chatterjee et al. have used supercritical carbon dioxide as reaction medium for the hydrogenolysis of diphenyl ether by carbon supported Rh, Pt, and Pd catalysts [131]. Furthermore, Rh/C showed a better performance than Pt/C and Pd/C catalysts in the hydrogenolysis of diphenyl ether. The CO₂ pressure and the presence of water strongly influence the performance of catalysts. Moreover, unsymmetrically substituted diaryl ether and alkyl-aryl ether compounds were investigated.

Song et al. tested Ni, Ru, and Pd nanoparticles supported over carbon in the hydrogenolysis of β -O-4 model compounds [132]. The selectivity to the C-O bond cleavage of the Ni/C catalyst was 85%, however, good conversions were also obtained by using Ru/C (40%) and Pd/C (69%) systems.

1.5 Valorization of lignin and its derived aromatic ethers through transfer hydrogenolysis processes

The lignin depolymerization and the cleavage of the C–O bond in aromatic ethers through the CTH approach has been demonstrated to be a valid alternative to classic hydrogenolysis procedures.

The lignin fraction was efficiently converted into dimeric and monomeric compounds via the CTH approach by several research groups and the main obtained results are reported in Table 1.2.

For example, Ford and co-workers demonstrated the occurrence of a single step process in the hydrogenolysis-depolymerization of the bio-oligomer organosolv lignin (obtained from sanded poplar sawdust) using a Cu-doped porous metal oxide (PMO) catalyst and supercritical MeOH (sc-MeOH) as H-source/solvent, at 300°C for 24h. A mixture of aromatics and monomeric substituted cyclohexyl derivatives with a low oxygen content was formed together with a gas phase mainly composed of H₂ (79% mol), CH₄ (8%), CO (9%) and CO₂ (4%) [133].

Barta and co-workers reported the dioxolv walnut lignin depolymerization using trifilic acid as catalyst in 1,4-dioxane at 140°C for 4 h. The main reaction products were C₂-aldehyde fragments [134].

Samec and co-workers, reported also the transfer hydrogenolysis of Pine sawdust, using Pd/C, as catalyst, and only an endogenous hydrogen source at 195°C for 1 h, converting its lignin content into aryl propene monomers. Formic acid generated from the organosolv process is the H-source used for the CTH reaction [135]. The same authors

studied also the transfer hydrogenolysis to transform the lignin to aromatic monomers using the Pd/C as catalyst and the hemicellulose fraction of a woody biomass as H-donor source to carry out the reactions [136]. Phenol, saturated and unsaturated propylphenols were obtained as the main reaction products and their selectivity was efficiently tuned by changing (i) the solvent biomass ratio and (ii) reaction temperatures/times. In another recent contribution, the Samec research group presented a three-step process to convert lignin to monomeric phenolic compounds and hydrocarbons by using the Pd/C catalyst in the CTH with carbohydrate fractions serving as hydrogen donors under mild alkaline conditions. The lignin obtained from the quercus suberin was converted with a selectivity of 90%. The advantage of suberin, as a potential biofuel feedstock, lies in its low oxygen content (10-15 wt%) [137].

In the 2017, the same authors presented for the first time a method to fractionate the lignin in high yield, to monophenolic products by a flow system in CTH conditions using the Pd/C catalyst and hemicellulose as internal H-source and a reducing agent at 160-220°C for 3-6 h. Furthermore, the cellulose fraction was found as solid residue in 92 wt% [138].

Also Sels and co-workers demonstrated that commercial Pd/C and Ru/C catalysts can be used in the CTH of lignin fractions (obtained from birch wood) using MeOH as H-donor solvent. They showed that Pd/C and Ru/C let to obtain different lignin products (4-n-propanolguaiacol and 4-n-propanolsyringol) at 250°C for 3h. The Ru/C catalyst favours the formation of para-propyl phenolics, while the Pd/C catalyst preferentially forms para-propanol phenol derivatives

with a remarkable selectivity (91%) to 4-n-propanolguaiacol (PohG) and 4-n-propanolsyringol (PohS). Finally, they demonstrated that the Pd/C catalyst is preferred when a high OH-content lignin oil is present [139].

Moreover, Kim and co-workers explored the potential efficiency of CTH using 2-propanol as solvent/H-donor to valorize the lignin-rich residue obtained from an ionic liquid conversion process, using Ru/C (5% wt) as catalyst. Monomeric and alkyl-substituted phenols (4-ethyl phenol, 2-methoxy phenol and phenol) were the main reaction products in the liquid oil, suggesting that the lignin residue can be efficiently depolymerized under CTH conditions [140].

The Song research group proposed a success method using the Ni/C catalyst in the presence of simple aliphatic alcohols as hydrogen source. Under mild reaction conditions (200 °C, for 6 h, 1 MPa Ar), the birch-wood lignin was converted into 4-propylguaiacol and 4-propylsyringol (M7S) with a selectivity of 97% and 54% yield referred to all monomers. They proposed that the lignin is first fragmented into smaller lignin species by alcoholysis reactions, and then the Ni/C catalyst fragments and converts the oligomers to monomeric phenols [141].

Table 1.2 A literature overview on the CTH of lignin promoted by heterogeneous catalysts.

Lignin type	Catalyst	H-source	Temperature [°C]	Main products	Ref.
Organosolv	Cu-MPO	Sc-MeOH	300	Cycloexyl derivates	[133]
Dioxolv	CF ₃ SO ₃ H	dioxane	140	aldehydes	[134]
Pine sawdust	Pd/C	Formic acid	195	Aryl monomers	[135]
Organosolv	Pd/C	Hemicellulose	210	Phenols, propylphenols	[136]
Organosolv	Pd/C	Hemicellulose	200	4-ethylguaiacol	[137]
Organosolv	Pd/C	Hemicellulose	220	Monophenolics	[138]
Organosolv	Pd/C	MeOH	250	Propanolguaiacol propanolsyringol	[139]
Organosolv	Ru/C	MeOH	250	phenolics	[140]
Organosolv	Ru/C	2-PO	300	phenols	[140]
Birch-wood	Ni/C	alcohols	200	propylguaiacol propylsyringol	[141]
Organosolv	Al-SBA-15	Tetraline, formic acid	140	Mesitol, syrangaldehyde	[142]
Organosolv	RANEY® Ni	Hemicellulose	220	Monocyclic products	[143]
Organosolv	RANEY® Ni	2-PO/H ₂ O	220	Arenes	[144]
Kraft	TiN-Ni and TiO ₂ -Ni	MeOH, EtOH, 2-PO, THF	150	Guaiacol products	[145]
Organosolv	Pd ₁ Ni ₄ /MIL -100(Fe)	H ₂ O	180	Phenols, guaiacols	[146]
Organosolv	FeB, NiB, FeNiB	sc-EtOH	320	depolymerization products	[147]
Kraft	Fe catalysts	2-PO/H ₂ O	373	hydrogenated cycles compounds	[148]
Organosolv	Cu-Mg-Al	sc-EtOH	340	C ₆₋₁₂ aromatics,	[149]

Toledano and Luque published a new microwave hydrogenolytic method (400 W at 140°C for 30 min) to depolymerise organosolv lignin, isolated from tree pruning, into simple phenolic compounds including mesitol and syringaldehyde by mild hydrogen-free conditions, using a range of bifunctional catalysts based on metal supported nanoparticles (Ni, Ru, Pd and Pt) on the mesoporous acidic aluminosilicate support (Al-SBA-15) with tetraline or formic acid as H-donor/ solvents. Among all catalysts, the Ni10%AlSBA gave the best degree of lignin depolymerization only after 30 minutes of reaction with the main products being bio-oil, bio-char and residual lignin [142].

Raney Ni can favour the organosolv separation promoting the upgrading of the liquor by means of a H-transfer process [143,144]. In analogy with studies conducted by the Samec research group, the hemicellulose fraction acts as H-donor substrate.

Conversely, Esposito et al. compared the effect of two different Ni-based systems (TiN-Ni and TiO₂-Ni) in the reductive depolymerization of Kraft lignin to substituted guaiacol products under mild conditions (at 150°C for ≈4.5 min) without molecular H₂ in a flow-reactor system. TiN-Ni shows a better catalytic performance than TiO₂-Ni, as a consequence of the major dispersion of Ni in the TiN phase. At the same time, the TiN-Ni system presents a better stability than the well-known Raney Ni and Pd/C catalysts [145].

Cai and co-workers reported the excellent catalytic performance of the Pd₁Ni₄/MIL-100(Fe) catalyst in the self-hydrogenolysis of organosolv lignin, using water as solvent, at 180°C for 6h. A 17% monomer yield and a set of reaction

products including substituted phenol and guaiacol derivatives were registered. The catalyst shows a highly porous structure, strong Lewis acid properties and water stability. Furthermore, the catalytic system can be recycled up to five times [146].

Chmely and co-workers, examined the catalytic activity of three different nanomaterial, amorphous B-containing FeNi alloys (FeB, NiB and FeNiB) in the transfer hydrogenolysis reaction of organosolv lignin using supercritical ethanol as H-source/solvent. FeNiB shows the best reactivity (74% conversion) and selectivity (84%) among the three catalysts affording 21 different depolymerization products [147].

Jin and co-workers described the depolymerization of the kraft lignin using a 2-propanol/water mixture system as solvent/hydrogen source over the Fe on Rh/La₂O₃/CeO₂-ZrO₂ catalyst at 373°C for 2 h. The main products obtained were C₁₂₋₂₆ aliphatic, C₆₋₁₆ aromatic and C₇₋₁₀ hydrogenated cyclic compounds [148].

Hensen et al investigated the role of different Cu-Mg-Al mixed oxides as catalysts, prepared on varying the Cu content and the CuMg/Al ratio, in the depolymerization of lignin in CTH conditions by using supercritical ethanol as solvent and H-donor molecules at 340°C for 4 h. The optimum performance was given by the mixture containing 20 wt% Cu and having a (Cu+Mg)/Al ratio of 4. Cu₂₀MgAl₍₄₎ affords the highest monomers yield and the least amount of repolymerization products during the lignin conversion [149].

The basic chemistry of the C-O bond breaking of aromatic ethers is still one of the fundamental tasks to

accomplish in order to selective produce chemicals from lignin under CTH conditions.

Prof. Ford research group can be surely considered one the first that studied the transfer hydrogenolysis of dihydrobenzofuran (DHBF), a lignin model compound (α -O-4 C-O bond), using the Cu-doped PMO as catalyst and MeOH as hydrogen source/solvent, in a microreactor, for 2 h at 300°C, in the presence of KOH. DHBF was fully converted to methylated 2-ethylphenols (63%), 2-ethylphenol (22%) and phenol (11%) [150].

Besse and co-workers investigated the catalytic transfer hydrogenolysis of eight model compounds with peculiar lignin linkages at 275-350°C in a batch reactor, using the Pt/C catalyst and a EtOH/H₂O mixture as hydrogen source solvent. They demonstrated that the lignin linkage cleavage follows the energy bond order showing that methoxyl and phenolic hydroxyl model molecules are unreactive, while α -1 model compounds are fully converted [151].

Han and co-workers recently demonstrated the high performing catalytic activity of the commercial Ru/C in CTH reactions of aromatic ethers using a variety of 4-O-5 type lignin model compounds using 2-propanol as solvent/H-donor under very mild conditions (at 120°C for 10-26 h) [152].

Samec and co-workers report that the commercial Pd/C can be a good catalyst in the C-O bond cleavage of the β -O-4' ether as model lignin molecule using formic acid and 2-propanol as H-donors. They also tested other heterogeneous catalysts (Ir/C, Ni/C, Pd/C, Re/C, Rh/C) and Pd/C shows the higher reactivity in the cleavage of β -O-4' C-O bond, allowing an efficient transformation to the corresponding aryl

ketones and phenols in high yield, at 80°C for 1-24h. They proposed a reaction mechanism in which the first key step is the dehydrogenation of the α -CHO group followed by formation of a Pd-enolate complex, that undergoes a transfer hydrogenolysis process [153, 154].

Wang et al., studied the CTH of phenol in presence of formic acid under mild reaction conditions: a good selectivity of 80% to cyclohexanone was observed in presence of Pd-based catalysts [155].

In 2012, Rinaldi and co-workers reported, for the first time, the use of the bimetallic RANEY® Ni catalyst in the H-transfer reactions of lignin model molecules under mild conditions. 2-propanol was used as reaction solvent and hydrogen source and 32 model substrates at temperatures from 80°C to 120°C for 3 h were thoroughly explored: the RANEY® Ni catalyst shows a high performance under CTH conditions and a good stability in the recycling tests [156]. In the course of years, his research group deeply investigated the CTH of other lignin model molecules, including phenol, in the presence of different heterogeneous catalysts elucidating also the role of the catalysts surface on the H-transfer mechanism [157, 158].

Kim and co-workers explained the CTH of guaiacol, another important lignin model compound, to cyclohexane (>70% yield) using the bimetallic RuRe/C catalytic system and 2-propanol as hydrogen source/solvent, demonstrating that the bimetallic catalyst is very efficient both in the dehydrogenation of solvent and the hydrogenation of guaiacol and that the presence of Re increases the rate of the C-O hydrogenolysis, allowing a higher selectivity to cyclohexane (\approx 60%) [159].

Finally, Wang and co-workers proposed a strategy for the direct deoxygenation of *p*-cresol to toluene (84% yield) via the catalytic transfer hydrogenolysis, promoted by the Ru/Nb₂O₅-SiO₂ catalyst using 2-propanol as hydrogen source/solvent at 230°C. Authors demonstrated the influence of *p*-cresol/2-propanol molar ratio on the toluene yield, in order to limit the hydrogenation of the aromatic ring. Furthermore, the efficiency of Ru/Nb₂O₅-SiO₂ catalyst on the CTH of other complex lignin model compounds (β -O-4 and α -O-4 linkages) was also studied [160].

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2

Aim of the thesis

Lignin, the most abundant natural phenolic biopolymer, is of particular interest for chemical industries since it is the only component that allows a sustainable production of aromatic compounds and intermediates [1-4].

In the last years, several strategies have been proposed for the lignin depolymerization into readily available aromatic compounds. Since the lignin sub-structure is characterized by large amounts of etheric bonds, catalytic reductive catalytic technologies (hydrogenolysis) have received strong attention, allowing the C-O bond breaking by adding molecular hydrogen.

However, the hydrogenolysis of lignin generally requires harsh reaction conditions due to the high dissociation energies involved in the C-O bond cleavage [5, 6]. Furthermore, the use of high pressure molecular hydrogen leads to undesired aromatic ring hydrogenated products, thus decreasing the process efficiency and lowering the degree of lignin depolymerization (fully saturated products are less susceptible to a further hydrogenolysis process).

In the last years, a significant growth towards an alternative catalytic approach avoiding the direct use of molecular hydrogen was considered. To this regard, the

catalytic transfer hydrogenolysis (CTH) technique represents a valid green alternative to classic hydrogenation/hydrogenolysis reactions owing to the use of indirect H-source molecules. Simple organic molecules including short chain alcohols (2-propanol, ethanol and methanol) can be efficiently used as H-donor for CTH reactions. At the same time, CTH molecules are generally easily to handle, potentially obtainable from renewable feedstocks and, due to their lower tendency to release hydrogen, may allow a higher production of aromatic compounds from lignin and its derived molecules.

Transition metals have been successfully used in the catalytic valorization of biomass-derived molecules. Traditionally, platinum-group metals (PGMm) are all excellent hydrogenation catalysts widely used in industry and refineries. Palladium has a lower expensive cost and more abundant natural reserves than platinum (that is still the most widely used element in catalysis). To this regard, the commercial Pd/C has attracted a lot of research interests allowing an efficient transformation of lignin and of a variety of aromatic ethers using formic acid and 2-propanol as H-donors

Moreover, palladium is characterized by a fundamental electronic configuration unique among transition metals ($4d^{10}, 5s^0$) that can be strongly influenced by the coordination environment. The presence of a secondary element, for example, may influence the electronic structure of palladium, the only transition metal that combines a full-filled d orbital with an empty frontier s orbital, leading to unusual catalytic properties different than those of monometallic Pd. Hence, heterogeneous catalysts based on palladium bimetallic

systems have gained increasing attention for their enhanced activity and durability in different reactions including the CTH of cellulose derived polyols.

As a consequence, the preparation of bimetallic Pd-based catalysts able to selective cleave the C–O bond in presence of aromatic functionalities together with a deep insight on the basic chemistry of aromatic ethers remains challenging to develop selective chemical processes to produce aromatics from lignin.

Therefore, the aim of this PhD work is the synthesis of bimetallic Pd-based catalysts (Pd-M with M = Fe, Ni and Co) prepared by the co-precipitation technique and their use in the transfer hydrogenolysis reaction of lignin and of its derived aromatic ethers by using 2-propanol as solvent/H-donor. All investigated catalysts were fully characterized through several physico-chemical techniques (XRD, TEM, H₂-TPR, XPS and EXAFS), in order to highlight the key factors that may affect the catalytic properties of the bimetallic palladium catalysts.

The transfer hydrogenolysis studies have been conceived with a bottom-up approach starting from the simplest lignin derived aromatic ethers, namely Benzyl Phenyl Ether (BPE), 2-Phenethyl Phenyl Ether (PPE) and Diphenyl Ether (DPE) as represented in Figure 2.0, to finally approach the lignin, with the aim to unravel the reactivity and selectivity, and to understand the mechanism of reactions involved.

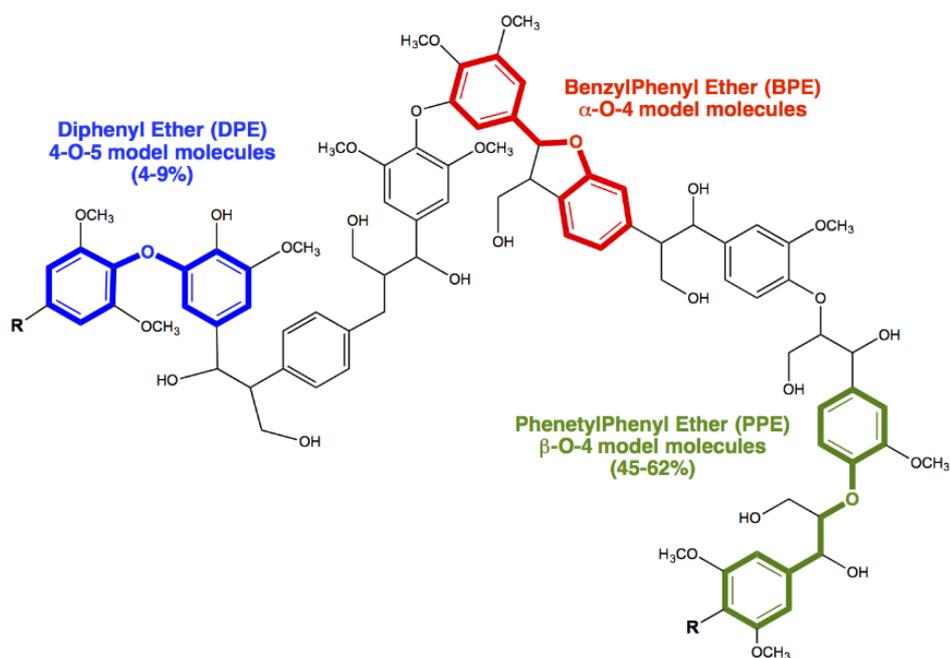


Figure 2.0 Benzyl Phenyl Ether (BPE), 2-Phenethyl Phenyl Ether (PPE) and Diphenyl Ether (DPE) as the simplest lignin-derived aromatic ethers.

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3

Experimental

3.1 Preparation of bimetallic Pd-based catalysts

All chemicals, involved in this doctoral experimentation, were purchased from commercial sources (Alfa Aesar, Sigma-Aldrich, Frinton Laboratories) and used without any further purification.

All catalysts, designed with a nominal palladium loading of 3-5 wt%, were prepared by the co-precipitation technique. A solution containing both nitrate precursors of palladium (II) and iron (III), cobalt (III) or nichel (II) were poured together into a solution of sodium carbonate (Figure 3.1).

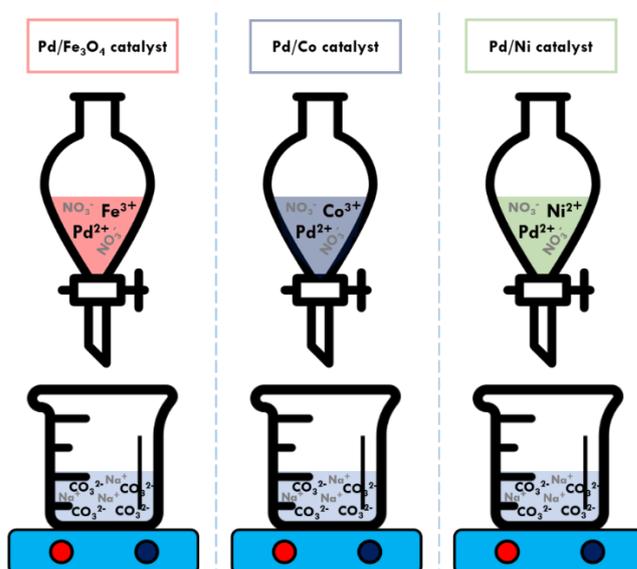


Figure 3.1 Co-precipitation of the metallic precursors within a solution of carbonates.

The ensuing co-precipitate was washed, filtrated and then dried overnight at 120 °C and, before any reaction, reduced with H₂ at 200 °C.

Benchmark catalysts such as Pd/C, PdO, Fe₃O₄, Co₃O₄, NiO were purchased from commercial sources (AlfaAesar and Sigma Aldrich) and Pd/C was used after a further reduction under H₂ flow at 200°C for 2h.

3.2 Characterization techniques

Analysis techniques, used for the characterization of heterogeneous bimetallic Pd-based catalysts, were those commonly used in catalysts studies: X-ray Diffraction (XRD), Transmission electron microscopy (TEM), Scanning electron microscopy (SEM), Temperature-programmed reduction (H₂-TPR), X-ray photoelectron spectroscopy (XPS) and X-ray absorption fine structure (EXAFS). The reported techniques provide accurate results useful to interpret the catalytic behaviour [1, 2].

3.2.1 X-ray Diffraction (XRD)

X-ray diffraction (XRD) is a powerful nondestructive structural analysis tool that has been used for decades for characterizing crystalline solids since they contain “matter periodically ordered”.

XRD data were collected using a Bruker D2 PHASER (Ni β -filtered Cu K α radiation with a λ of 1.54 Å) in the 2 theta range of 20–80° (scan speed of 0.5° min⁻¹) [3, 4].

3.2.2 Transmission Electron Microscopy (TEM)

The Transmission Electron Microscopy (TEM) technique provides most of the necessary fundamental information on morphology and microstructure of the material.

Transmission Electron Microscopy (TEM) measurements were carried out using a JEM-2100F (200 kV).

The mean particle size and relative particles distributions were calculated from the expression:

$$d_n = \sum n_i d_i / n_i$$

(n_i = number of particles having a diameter d_i) [5-8].

3.2.3 Scanning Electron Microscopy

The Scanning Electron Microscopy reveals interesting informations about a given sample including external morphology, chemical composition, and crystalline structure.

Scanning Electron Microscopy measurements were carried out using a Phenom Pro-X scanning electron microscope, equipped with an energy-dispersive x-ray spectrometer (EDX), an analytical technique, used for the elemental analysis or chemical characterizations, and in order to evaluate the content and the dispersion of metals, acquiring, for all samples, at least 20 points for 3 different magnifications.

3.2.4 Hydrogen Temperature Programmed Reduction (H₂-TPR)

The hydrogen temperature-programmed reduction (H₂-TPR) is a widely used technique that allows to find the best reduction conditions for heterogeneous catalysts [9]. It is based on heating a sample, through a linear temperature ramp in a hydrogen stream, to obtain a fingerprint profile of the sample reducibility that shows the influence of the

support and eventual promoters. Furthermore, the amount of hydrogen consumed allows to determine the quantities of reducible species. Consequently, in heterogeneous Pd-M catalysts, the H₂-TPR is a simple and formidable tool to investigate the reduction behavior as well as the interaction between palladium and other metallic species.

H₂-TPR reductions were carried out using a TPR instrument equipped with a TCD detector. The dried catalyst (50mg) was heated at a constant rate of 10 °C min⁻¹ from 0 to 1000 °C in a 5 vol % of H₂/Ar mixture at a flow rate of 20 cm³ min⁻¹.

3.2.5 X-ray Photoelectron Spectroscopy (XPS)

The X-ray photoelectron spectroscopy (XPS) allows to study the materials surface properties, permitting to know the chemical composition and to establish involved bonds and oxidation metal states [10-12]. It is based on the irradiation of a sample with a monochromatic x-ray source: photons enter the material and undergo various interactions, leading to the photoelectric effect and the Auger emission. In both cases, an electron is ejected from the material with a given kinetic energy that allows information on energies involved on internal electrons of the case materials.

XPS data were collected using a JPS-9010MC photoelectron spectrometer (radiation source = Al K α - 1486.6 eV). The catalyst was previously reduced and then inserted into the chamber instrument, preventing any contact with air.

XPS data of “in situ-reduced” catalysts were obtained after a further in-situ thermal treatment in a secondary reduction chamber at 200°C under a hydrogen pressure of

100 Pa for 4 hours. All data were always obtained using a room temperature, and the binding energies (BE) were calibrated taking as reference the C 1s peak (284.6 eV).

3.2.6 Extended X-ray Absorption Fine Structure (EXAFS)

The Extended X-ray absorption fine structure (EXAFS) can provide valuable data about the structure of metal alloys, since it is the only spectroscopic technique that gives information on the local structure around Pd, the Pd-support oxide interaction and/or the Pd bimetal nanoparticle formation in our systems [13-15].

EXAFS data of the Pd-based catalysts have been measured at the Photon Factory of the High Energy Accelerator Research Organization - KEK (Tsukuba, Japan). Fe-K edge XANES/EXAFS spectra for the catalysts were obtained using a Si (111) two-crystal monochromator with beam line BL9A whereas Pd K-edge spectra were obtained using a Si (311) two-crystal monochromator with beam line NW10A.

Analysis of EXAFS data have been performed using the EXAFS analysis program “REX” (Rigaku Co.).

3.3 Organosolv process

The olive tree pruning was mechanically pretreated in a planetary ball milling (500 rpm for 10 min) and utilised as feedstock to isolate lignin. The treatment for lignin extraction consisted on the digestion of the feedstock in a mixture of ethanol-water (70 wt.%) at 210 °C for 90 min [16-19] in a pressure reactor.

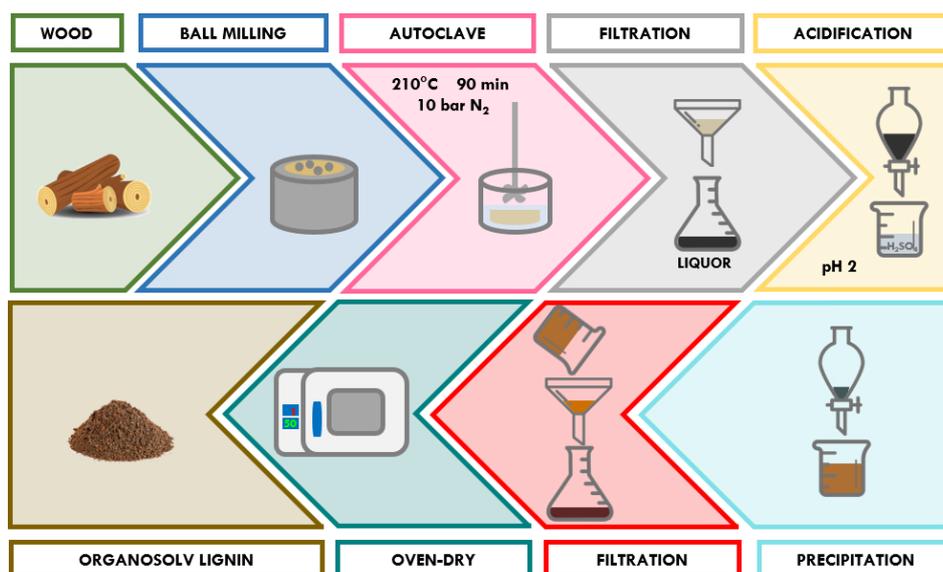


Figure 3.2 Schematic representation of the organosolv process from olive tree pruning.

The liquid fraction (where lignin was dissolved) was separated from the solid fraction by filtration. Dissolved lignin was isolated by precipitation with two acidified portions of an aqueous solution (pH around 2). The obtained solid was filtered and then dried overnight at 50 °C. A schematic representation of the adopted organosolv process is reported in Figure 3.2.

3.4 Catalytic experiments

Reactions were performed at 500 rpm in a 160 mL or 100 mL stainless steel autoclave (Parr Instrument - 4560 Mini reactor system). The reactor was loaded with the desired catalyst (0.125-250 g) suspended in a solution containing the substrate solution in 2-propanol (40-60 mL, 0.1 M). Any trace of air present in the system was eliminated by fluxing three times N₂ (99.99%). The reactor was subsequently pressurized at the desired gas (N₂ or H₂) pressure and heated at the final reaction temperature (180-240 °C). At the end of the reaction, the system was cooled down at room

temperature, the pressure released and the analysis of the organic phase was done by gas chromatography or, in the case of the CTH lignin, by 2D HSQC NMR analysis.

For every recycling test, after any run, the catalyst was magnetically recovered, thoroughly washed with 2-propanol and reused under the same reaction conditions.

3.5 Analytical techniques applied to reactions

Products present in the organic liquid phase, were quantified through the Gas Chromatography (GC) analysis and, in the case of lignin CTH, by 2D HSQC NMR analysis.

Gas chromatographic analyses were performed on an Agilent 6890N gas chromatograph equipped with a wide-bore capillary column (CP- WAX 52CB, 60 m, i.d. 0.53 mm) connected with a FID detector (Flame Ionization Detector).

The conversion and product selectivity in the liquid phase were calculated on the basis of the following equations:

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

$$\text{Liquid phase selectivity [\%]} = \frac{\text{mol of specific product}}{\text{sum of mol of all products}} \times 100$$

The products yield was calculated and defined as:

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

$$\text{Aromatic Yield [\%]} = \frac{\text{sum of mol of aromatic products}}{\text{mol of substrate feed}} \times 100$$

Number average molecular weights (Mn) of the organosolv lignin and the relative mixture of reaction products were determined in DMF solution by GPC using

HPLC Lab Flow 2000 apparatus, equipped with an injector Rheodyne 7725i, a Phenomenex Phenogel 5- μ m MXL column and an UV-VIS detector Linear Instruments model UVIS-200, working at 254 nm at Dipartimento di Chimica Industriale “Toso Montanari”, Università degli Studi di Bologna (Bologna, Italy). The calibration curve was obtained with standard monodisperse polystyrene samples.

2D-HSQC NMR analyse were performed at Dipartimento di Ingegneria Civile, Ambientale, del territorio, Edile e di Chimica, Politecnico di Bari (Bari, Italy) on a Bruker Avance III 700 MHz UltraShield Plus NMR spectrometer equipped with a 5 mm inverse probe and with an autosampler, using a 4.0 mm HX MAS probe at 298 K.

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4

Physico-chemical characterization of investigated bimetallic catalysts

4.1 X-ray Diffraction (XRD)

XRD patterns of co-precipitated bimetallic Pd-based catalysts are depicted in Figure 4.1.

The pattern of Pd/Fe₃O₄, after the reduction at 200°C under H₂ flow, exhibits only peaks related to Fe₃O₄ and no metallic palladium peaks were observed, indicating the presence of very small palladium particles highly dispersed [1-7]. Typical diffraction peaks related to the cubic crystal magnetite, in agreement with the Joint Committee on Powder Diffraction Standards (JCPDS), were found: 30.4° (220); 35.8° (311); 43.4° (400); 54.0° (422); 57.5° (511); 63.2° (440) [8-10]. Furthermore, the absence of the (111) reflection, related to metallic palladium at $2\theta=40.2^\circ$, means that palladium nanoparticles are very well dispersed over the catalyst surface [1].

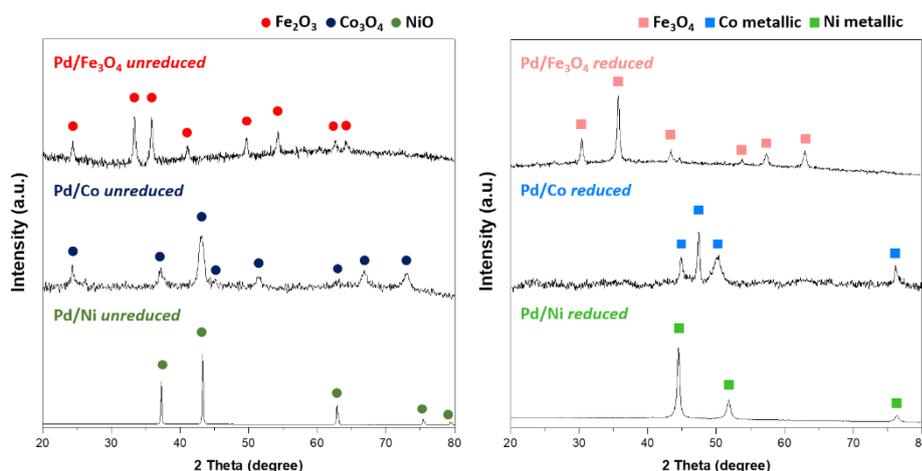


Figure 4.1 XRD patterns of bimetallic Pd-based catalysts.

The X-ray powder diffraction (XRD) pattern of the unreduced Pd/Co catalyst shows diffraction peaks typical of the pure cubic crystalline Co_3O_4 [11]. After reduction, diffraction peaks of metallic cobalt can be easily observed indicating the promoting effect of Pd in the support reduction. This point is worth of remark since the complete reduction of Co_3O_4 into metallic Co in H_2 atmosphere generally occurs up to 400°C [12]. Moreover, the absence of the Pd (111) diffraction peaks is indicative of highly dispersed palladium particles as confirmed also by SEM-EDX analysis [6].

XRD pattern of the Pd/Ni catalyst, after the reduction at 250°C under H_2 flow, shows peaks related to the reduction of NiO into metallic nickel. The typical diffraction peak of the metallic Pd (111) at $2\theta = 40.18^\circ$ was not observed suggesting the presence of extremely small and well-dispersed palladium particles. Typical diffraction lines at 2θ values of classic metallic Ni (44.4° 51.8° , 76.2°), in good agreement with previous reports [5, 13-14] are also observed, indicating the presence of a Pd/Ni alloy phase.

4.2 Transmission Electron Microscopy (TEM)

TEM images of investigated bimetallic Pd-based catalysts are reported in Figure 4.2.

The bimetallic Pd/Fe₃O₄ catalyst shows a predominance of extremely small palladium particles. A relatively narrow particles sizes distribution with diameter values ranging between 0.5 and 2.5 nm, with a majority of particles of 1.2 nm diameter, followed by a second population of slightly larger palladium particles, with 2.3 nm average diameter, was found [1], in perfect agreement with XRD results, that suggest the presence of highly dispersed palladium particles, which should be extremely small, being the conventional limit of XRD instruments, for the detection of supported nanoparticles, usually in the range of 2-2.5 nm.

Representative TEM images of the reduced Pd/Co catalyst are reported in Figure 4.2 where distinctive lattice fringes with an interplanar distance of 0.19 nm, typical of the (111) plane of the metallic cobalt [15], can be easily detected confirming the complete reduction of the support. Smaller darker nanoparticles were identified, as bimetallic Pd-Co ensembles [16-17] with a particles size distribution of about 8.7 nm.

A representative TEM analysis of the Pd/Ni system reveals faceted Ni metal particles and small palladium ensembles with a narrow particles size distribution.

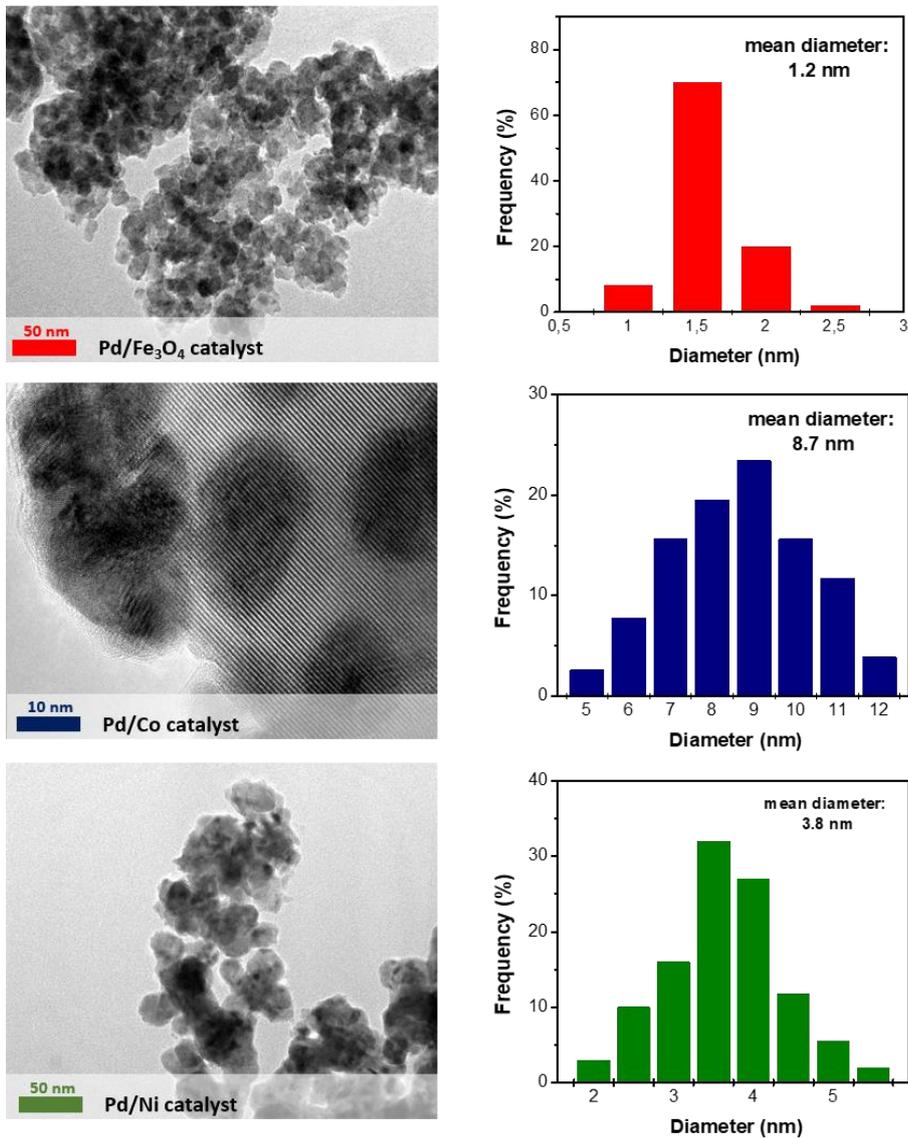


Figure 4.2 TEM images of Pd-based catalysts at 50 and 5 nm and their relative particle size distribution.

4.3 Scanning Electron Microscopy (SEM)

Results of SEM-EDX analysis of reduced Pd/Fe₃O₄, Pd/Co and Pd/Ni catalysts, including elemental mapping, are depicted in Figure 4.3. Highly dispersed palladium particles are easily detected by SEM-EDX analysis in all investigated systems.

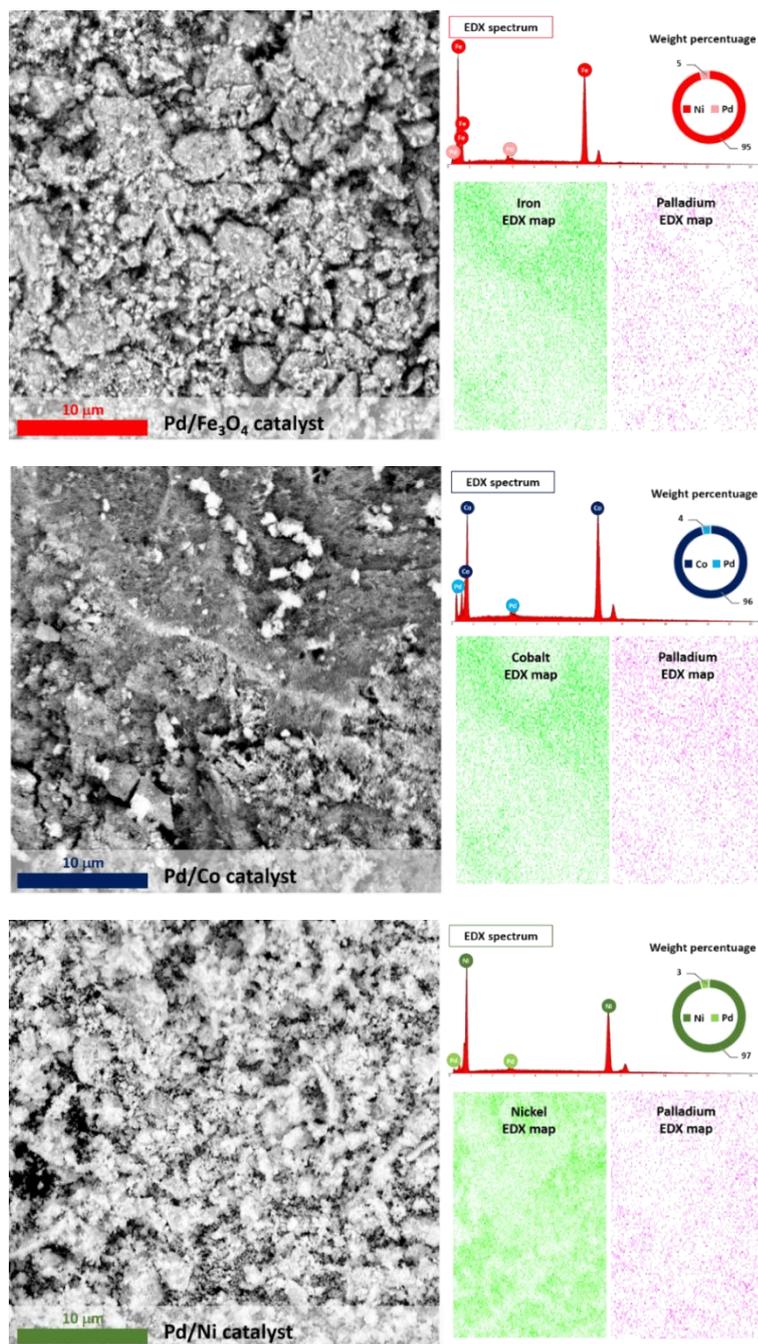


Figure 4.3 SEM images of Pd-based catalysts.

4.4 Hydrogen Temperature Programmed Reduction (H₂-TPR)

H₂-TPR profiles of our catalysts are shown in Figure 4.4.

The H₂-TPR profile of the unreduced co-precipitated Pd/Fe₃O₄ catalyst shows a main area containing only one intense peak of reduction at low temperature, starting at 44°C and centered at ca. 80°C, that includes reductions of either Pd⁺² → Pd⁰ and Fe⁺³ → Fe₃O₄, as determined by the calculation of the hydrogen consumption [1].

The H₂-TPR profile of the unreduced pure Fe₂O₃ catalyst is also included, in order to compare the reductive profile of both the bimetallic catalyst and that of the iron oxide (Figure 4.4). For the pure iron oxide (Fe₂O₃), the reduction starts at significantly higher temperatures (ca. 320°C) and the profile presents two main peaks: the first centered at ca. 420°C that belongs to the reduction of Fe⁺³ → Fe₃O₄, whilst the second is centered at ca. 690°C due to the following reduction of Fe₃O₄ → FeO.

The promoting effect played by palladium nanoparticles on the iron oxide support, reduction is very clear and is indicative of a strong metal-support interaction (SMSI) [1, 3]. Other authors, report similar results and underline the role of the coprecipitation method on the effectiveness of palladium to promote the support reduction [1, 3-4, 18-19].

Again the H₂-TPR profile of the Pd/Co sample is characterized by only one broad and intense peak centred at about 260°C, that can be related to the simultaneous reduction of both palladium and cobalt cations.

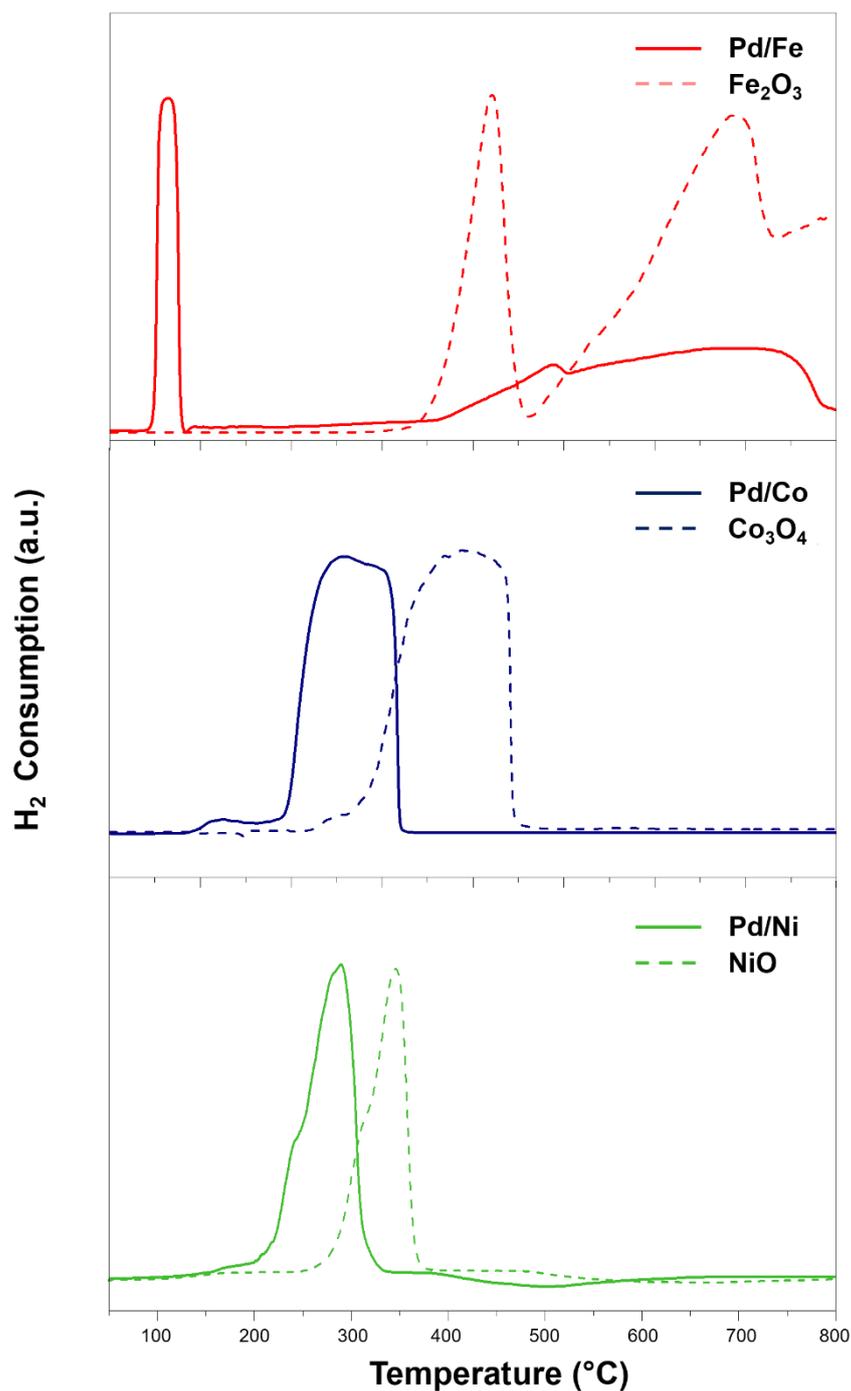


Figure 4.4 H₂-TPR profiles of Pd-based catalysts and their corresponding metal oxide supports.

Most important, the main H₂-TPR reduction peak of the Pd/Co sample (Figure 4.4) is shifted to lower temperatures of about 150°C with respect to that of the pure Co₃O₄ sample,

prepared by the identical synthetic procedure (coprecipitation) and is characterized, in analogy with other reports, by a wide non symmetric peak that includes both $\text{Co}_3\text{O}_4 \rightarrow \text{CoO}$ and $\text{CoO} \rightarrow \text{Co}$ reductions [20-21].

This phenomenon is well known and is commonly ascribed to the promoting effect of well-dispersed palladium particles on the Co_3O_4 reduction indicating a strong interaction between Pd ions and the metal oxide support [22].

The H_2 -TPR profile of NiO (Figure 4.4) displays an intense reduction peak centered at ca. 350 °C corresponding to the reduction step of nickel oxide, with a shoulder at 310 °C, assigned to the reduction of oxygen species adsorbed on the surface [23, 24]. On the other hand, the H_2 -TPR profile of Pd/Ni (Figure 3.3) is analogous to that of the NiO sample although the center of the main reduction peak is shifted to around 280 °C and displays the reduction of both Pd and Ni ions, indicative of a promoting effect of well-dispersed Pd particles on NiO reduction [2,21].

4.5 X-ray Photoelectron Spectroscopy (XPS)

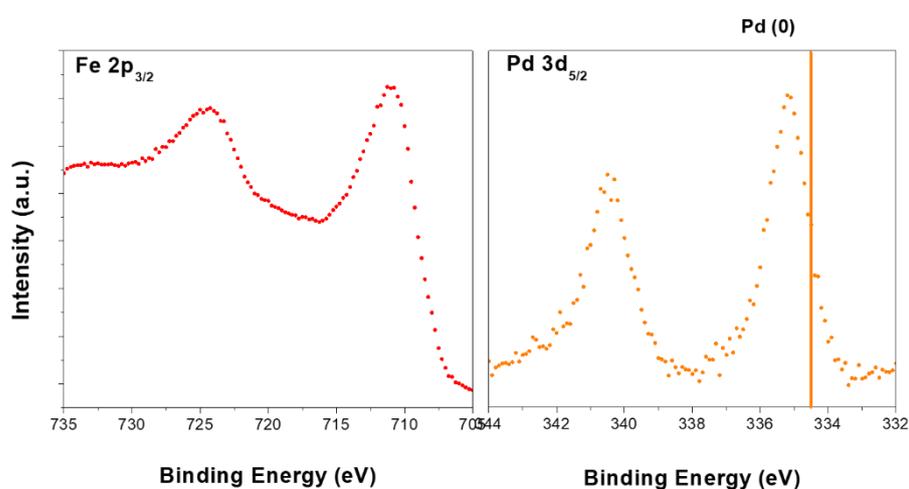
The XPS analysis helps to understand the electronic properties of investigated bimetallic catalysts. All peaks were analyzed by curve-fitting and the results are summarized in Table 4.1.

XPS spectra of reduced and unreduced Pd/ Fe_xO_y samples confirm the presence of only Fe_3O_4 as oxide support (Figures 3.5). The datum is inferred from the absence of the satellite peak at 718.5 eV, that indicates the absence of the Fe_2O_3 structure over the reduced surface (Table 4.1).

Table 4.1 Binding Energy values of Pd 3d_{5/2}, Fe 2p_{3/2} and Fe 2p_{3/2} sat., Co 2p_{3/2} and Co 2p_{3/2} sat. Ni 2p_{3/2} and Ni 2p_{3/2} sat. for *un*-reduced and reduced investigated Pd-based catalysts.

Catalyst	Binding Energy (eV)			
	Pd 3d _{5/2}	Fe 2p _{3/2}	Co 2p _{3/2}	Ni 2p _{3/2}
Pd/Fe₃O₄	335.3	710.7	-	-
Pd/Fe <i>unred</i>	336.6	710.9	-	-
Pd/Co	335.5	-	778.2	-
Pd/Co <i>unred</i>	336.8	-	779.9	-
Pd/Ni	335.6	-	-	852.2
Pd/Ni <i>unred</i>	336.8	-	-	853.7
Pd/C	335.0	-	-	-
Pd/C <i>unred</i>	336.6	-	-	-

Furthermore, after the reducing treatment, the shift of ca. 0.5 eV of the Pd 3d_{5/2} binding energy to higher values, than that observed for metallic palladium, indicates the presence of partial positively charged metal Pd species (Pd^{δ+}) (Table 4.1 and Figure 4.5). This evidence is attributed to alloy formation in bimetallic supported Pd catalysts [2].

**Figure 4.5** XPS of the Pd/Fe₃O₄ catalyst

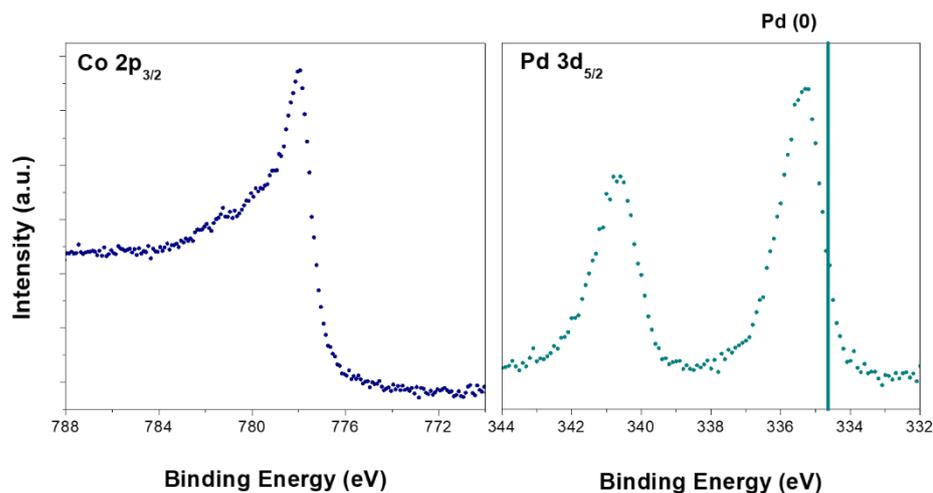


Figure 4.6 XPS of Pd/Co catalyst

The XPS spectrum of the reduced Pd/Co catalyst shows that the binding energy of the Pd 3d_{5/2} level appears at about 0.7 eV value higher than that of the binding energy of metallic palladium, indicating the presence of partial positively charged Pd species, suggesting the formation of a Pd-Co alloy (Figure 4.6) [25-26]. At the same time, the presence of metallic cobalt is confirmed by its typical sharp peak at 778.2 eV [27].

XPS results of unreduced, reduced, and in situ reduced Pd/Ni samples were also achieved. Unreduced Ni and Pd/Ni samples display, in the Ni_{2p_{3/2}} area, peaks centered at about 853.6, 855.2, and 856.5 eV corresponding to NiO and Ni(OH)₂ species [28]. In the reduced Ni catalyst, the peak at 852.6 eV, typical of metallic Ni, is detected. After in situ reduction at 200 °C, the binding energy of Ni_{2p_{3/2}} is characterized by a shift to lower BE values of about 0.8 eV with respect to that of pure nickel. This can be ascribed to an electron density transfer from Pd to Ni species [29].

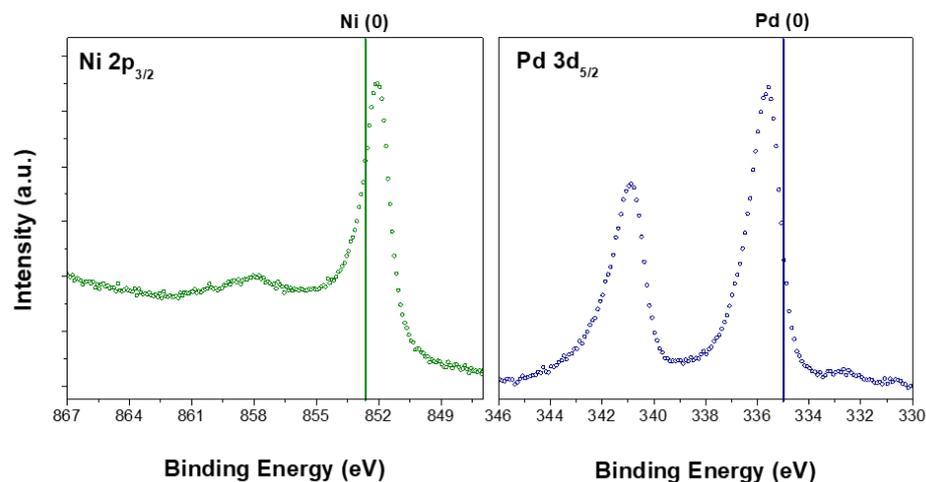


Figure 4.7 XPS of Pd/Ni catalyst

Accordingly, in reduced and in situ reduced PdNi systems the binding energy of the Pd_{3d_{5/2}} level was found at 335.6 eV, about 0.5 eV higher than that reported for metallic palladium (Figure 4.7), confirming the formation of a bimetallic Pd/Ni ensemble that might be an alloy [30].

4.6 Extended X-ray Absorption Fine Structure (EXAFS)

The results, obtained for all investigated Pd-based catalysts are reported in Table 4.2.

Table 4.2 X-ray absorption fine structure characterization at the Pd K-edge for investigated Pd-based catalysts.

Catalyst	Scattering Pair	CN	R [Å]	DW [Å]	R [%]
Pd/Fe	Pd-Pd	2.59	2.71	0.091	2.0
	Pd-Fe	0.78	2.51	0.047	1.0
Pd/Co	Pd-Pd	0.3	2,69	0,021	1,9
	Pd-Co	3,92	2,51	0,047	0,8
Pd/Ni	Pd-Pd	-	-	-	-
	Pd-Ni	2.55	6.3	0,070	0.7
Pd/C	Pd-Pd	2.73	8.0	0.061	2.6

CN: Coordination number; **R:** Interatomic distance; **DW:** Debye-Waller factor

The EXAFS characterization of the reduced Pd/Fe₃O₄ catalyst reveals that some iron particles are alloyed into the palladium nanoparticles forming Pd-Fe bimetallic ensembles, since the Pd-Fe bond length is shorter than that of Pd-Pd bonds (Table 4.2) and indicate that, on the Pd/Fe reduced catalyst, strong interactions between palladium nanoparticles and the iron oxide support occur [1,2].

On the other hand, results of extended X-ray absorption fine structure (EXAFS)(Table 3.2) relative to the Pd/Co sample reveal also a shorter scattering Pd-Co path of 2.51 Å compared with that of the Pd-Pd distance of about 2.70 Å confirming the formation of Pd-Co bimetallic ensembles [31,32].

Also the Pd-Ni catalyst is characterized by a shorter Pd-Ni distance. However, the main peculiarity, in the PdNi sample, is the lack of any Pd-Pd scattering path and this implies the much higher concentration of Ni in the Pd-Ni alloy.

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5

Catalytic valorization of lignin and its derived aromatic ethers promoted by the bimetallic Pd/Fe₃O₄ system

5.1 Catalytic transfer hydrogenolysis of benzyl phenyl ether

In Table 5.1 results obtained from the catalytic transfer hydrogenolysis of benzyl phenyl ether (BPE) promoted by the bimetallic Pd/Fe₃O₄ and the Pd/C catalysts, at 90 minutes of reaction time, using 2-propanol as H-donor, within the range of temperature investigated (180-240°C), in presence of a very low initial N₂ pressure (5 bar) are summarized.

In the presence of the heterogeneous Pd/Fe₃O₄ catalyst, at 240 °C and within 90 minutes, BPE is fully converted (100% conversion) to toluene and phenol as the only reaction products (100% aromatic yield).

Table 5.1 Transfer hydrogenolysis of aromatic ethers in the presence of Pd/Fe₃O₄ and Pd/C catalysts. Conditions: 0.25 g of catalyst; 60 ml of the entry solution – BPE 0.1 M; 10 bar N₂; 90 min.

Catalysts	Temperature	Conversion	Aromatic Selectivity
	[°C]	[%]	[%]
Pd/Fe ₃ O ₄	240	100	100
Pd/C	240	8	100
Pd/Fe ₃ O ₄	210	49	100
Pd/C	210	4	100
Pd/Fe ₃ O ₄	180	20	100
Pd/C	180	-	-

Indeed on using Pd/Fe₃O₄ as catalyst and 2-propanol as H-source, an appreciable BPE (0.1 M) conversion (19.7%) was achieved at temperature as low as 180 °C (Table 5.1). The conversion of BPE increases on increasing the reaction temperature and it is fully converted into phenol and toluene at 240 °C. Cyclohexane and methyl cyclohexane were not detected, clearly indicating that the cleavage of the etheric C–O bond occurs as the primary reaction route under the reaction conditions adopted.

On the other hand, Pd/C was found to be not active in C–O bond breaking at 180 °C (0% conversion) under CTH conditions, while, at 210 °C and 240 °C, a very low conversion of BPE was achieved (Table 5.1).

In order to verify the low tendency of the Pd/Fe₃O₄ catalyst to hydrogenate the aromatic ring, phenol and toluene were allowed to react in the same reaction conditions as those employed for BPE. In both cases, products deriving from aromatic ring hydrogenation were not observed.

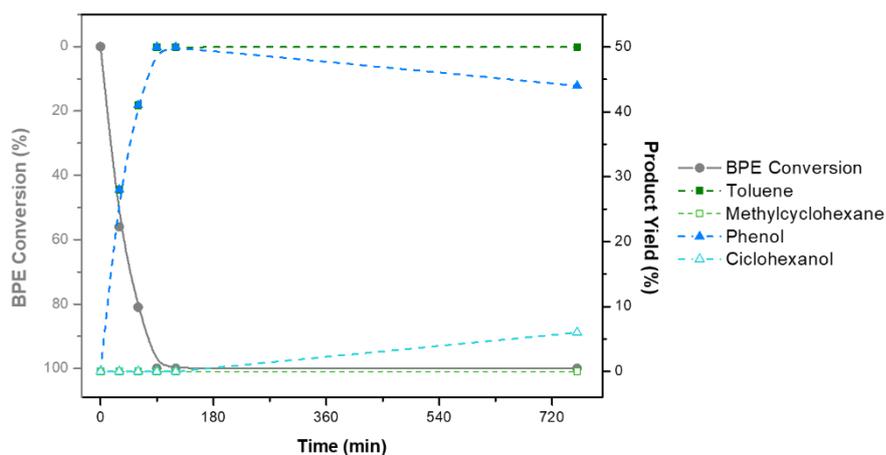


Figure 5.1 Reaction time effect on the BPE conversion (%) and liquid products selectivity (%) in the CTH at 240 °C.

The ability of the bimetallic Pd–Fe system in the C–O bond breaking without parallel hydrogenation of the aromatic ring is explained on the basis of a strong adsorption preference of the aromatic ring onto exposed Fe atoms [1-3].

Having identified 240 °C as the best reaction temperature in order to obtain aromatics from BPE, the CTH of benzyl phenyl ether at different reaction times (Figure 5.1) was investigated.

The BPE conversion increases on increasing the reaction time, when passing from 30 to 90 min. However the selectivity to phenol slightly decreases after 12 hours, as a result of further hydrogenation to cyclohexanol (Figure 5.1), in agreement with other studies that report a much higher hydrogenation rate of phenol than that of toluene [4].

Results relative to the CTH experiments carried out at 180 and 210 °C at different reaction times are summarized in Table 5.2.

Table 5.2 Reaction time effect on the BPE conversion (%) and aromatic selectivity (%) in the CTH at 180 and 210°C promoted by the Pd/Fe₃O₄ catalyst (0,25 g catalyst; 60 ml entry solution 0.1 M; 10 bar N₂).

Temp. [°C]	Time [h]	Conversion [%]	Aromatic Selectivity [%]
210	12	100	99,0
210	6	100	100
210	3	81,4	100
180	12	41,0	100
180	6	40,0	100
180	3	30,2	100

Cross-check experiments, carried out under the same reaction conditions (240 °C, 90 min, 10 bar N₂), show also that both the presence of pure Fe₃O₄ as well as metallic Fe and the absence of any catalyst (non-catalyzed pyrolysis conditions) do not give any BPE conversion, implying that the presence of palladium is essential for the C–O bond breaking.

Catalyst recycle tests using the Pd/Fe₃O₄ catalyst at 240 °C was performed and a BPE conversion up to 80% after 8 recycling tests, is observed, highlighting the good stability of the catalyst (Figure 5.2). Products selectivity, at the same time, does not change appreciably.

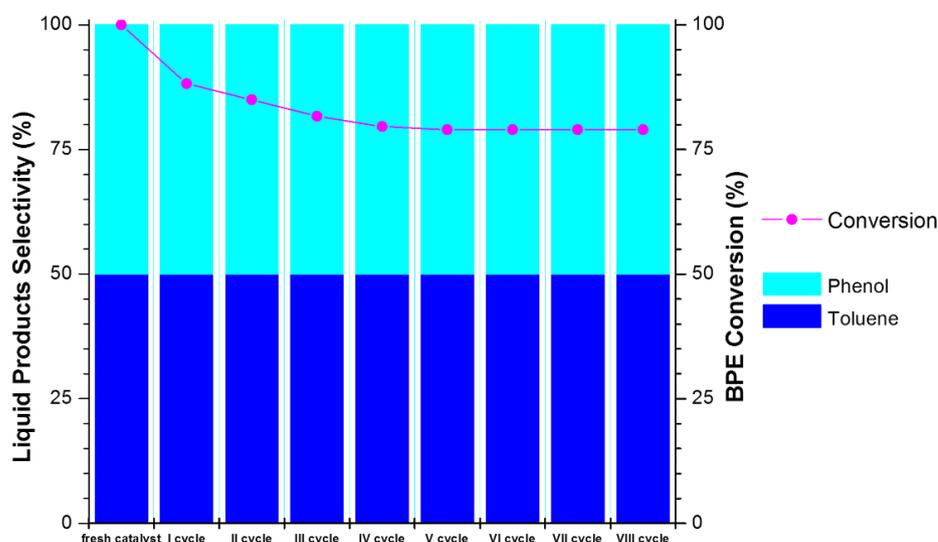


Figure 5.2 Recycle of the Pd/Fe₃O₄ catalyst in the transfer hydrogenolysis of BPE (240°C; 90 min; 0,25 g catalyst; 60ml entry solution 0.1 M; 10 bar N₂ pressure).

5.1.1 Hydrogenolysis reactions

For a comparison, the C–O bond breaking of BPE was also studied in the presence of molecular H₂ (10 bar) and results are summarized in Table 5.3.

A decrease of BPE conversion (75.0%) is observed, which can be ascribed to the competitive adsorption of the substrate and H₂ on the catalyst surface as previously observed in other hydrogenolysis reactions over heterogeneous palladium systems [5-7].

On increasing the initial H₂ pressure to 20 and 40 bar, keeping the temperature at 240 °C, the conversion of BPE does not change significantly and the selectivity to arene derivatives remains above 98% (Table 5.3), thus confirming the low tendency of the Pd/Fe₃O₄ catalyst to hydrogenate the aromatic ring.

Table 5.3 Hydrogenolysis of BPE promoted by the Pd/Fe₃O₄ catalyst (0,25 g catalyst; 90 min, 60 ml entry solution 0.1 M).

H₂ pressure	BPE Conversion	Aromatic Selectivity
[bar]	[%]	[%]
10	75	100
20	73	100
40	71	98

Conversely, in the presence of Pd/C, under hydrogenolysis conditions (240 °C, 90 min, 10 bar H₂), the reaction affords a 98% conversion. However a mixture including ring hydrogenated products was obtained with an aromatic selectivity of 40%. These results suggest that, the poor performance of the Pd/C catalyst in CTH reactions can be related to its lower ability to dehydrogenate 2-propanol as revealed by the very small amount of acetone detected at the end of the reaction [8].

5.1.2 Screening of different Hydrogen sources

The H-donor ability of simple primary (methanol, ethanol, 1-propanol, 1-butanol and 1-pentanol) and secondary (2-butanol, 2-pentanol and 3-pentanol) alcohols with different carbon chain lengths was tested (Table 5.4).

A tight correlation between the moles/l of aldehyde or ketone formed (H-donor ability) and the amount of BPE converted (moles/l) was found.

Noteworthy, with the exception of 2-propanol, secondary alcohols are generally less effective in the CTH of BPE.

Table 5.4 Transfer hydrogenolysis of BPE in the presence of the Pd/Fe₃O₄ catalyst (0.25 g of catalyst; 60 ml of entry solution; 240 °C; 10 bar N₂; 90 min) using simple primary and secondary alcohols as reaction solvents.

Solvent	Dehydrogenation (mol/l)	H-ability (mol/l)	Conversion (mol/l)
Methanol	-	-	0.003
Ethanol	0.015	0.021	0.016
1-propanol	0.045	0.060	0.057
1-Butanol	0.050	0.057	0.052
1-Pentanol	0.050	0.058	0.055
2-Propanol	0.240	0.120	0.100
2-Butanol	0.090	0.038	0.035
2-Pentanol	0.080	0.019	0.019
3-Pentanol	0.075	0.002	0.002

This is in remarkable contrast with the alcohols dehydrogenation ability (the secondary alcohol is more active than the primary one, due to the higher electron-releasing inductive effect). Hence, the reactivity of the same pure alcohols in the presence of the Pd/Fe₃O₄ catalyst has been also investigated under the same reaction conditions (240 °C, 90 min, 10 bar N₂) in order to determine their dehydrogenation capability in the absence of the substrate (Tab. 5.4).

In this case, the amount of aldehydes, formed from the primary alcohols, is slightly lower than that measured in the presence of BPE, suggesting that even though hydrogen can be transferred to the metal surface, the direct transfer of the donor solvent to BPE proceeds a little bit faster. Most important, the well-known higher tendency of secondary alcohols to release hydrogen was confirmed [9, 10]. Noteworthy, the amount of ketones formed is by far higher than that obtained in the transfer hydrogenolysis of BPE.

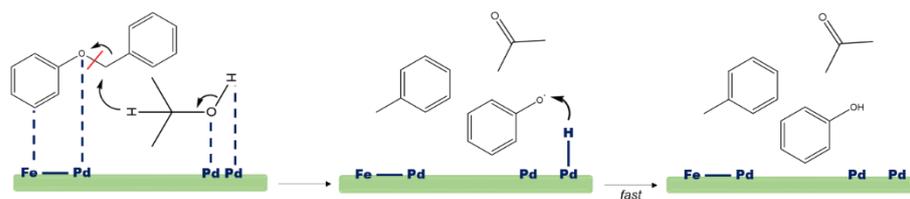
These results, considered all together, suggest that the CTH process of BPE is very sensitive to the steric hindrance of the H-donor molecule. Such a conclusion, coupled with the close relationship between the molar amount of carbonyl derived compounds and that of the converted BPE, suggests that the H-transfer from the alcohol and the hydrogen promoting the C–O bond breaking occur in a unique chemical process.

5.1.3 The CTH Reaction Mechanism

The formulation of a possible reaction route has to take also into account (i) the spectroscopic evidence of Pd–Fe site formation on the catalyst surface and (ii) the computational results of the hydrodeoxygenation of some lignin derived compounds (phenol, guaiacol, cresols, etc.) on the Pd–Fe/C catalyst that show a favourable adsorption of the aromatic ring on the Fe atoms while H₂ preferentially adsorbs and dissociates on the Pd entities [1-3].

Therefore, the most convincing reaction mechanism (Scheme 5.1) suggests the previous adsorption of BPE on the Fe–Pd bimetallic sites in which the aromatic ring is exposed into the Fe surface with oxygen stabilized on partial positively charged palladium [1-3, 11].

At the same time, 2-propanol is adsorbed on palladium sites (either “free” Pd metallic centers or those belonging to the bimetallic Pd–Fe ensemble) with its hydroxyl group, making possible the subsequent transfer of the α -hydrogen atom to the α -methylene moiety of BPE, thus weakening the etheric C–O bond and allowing its consequent cleavage.



Scheme 5.1 CTH mechanism of BPE promoted by Pd/Fe₃O₄ catalyst in presence of 2-propanol as H-donor/solvent.

This step, recently demonstrated by experimental/theoretical studies on CTH reactions [12–14] is deeply influenced by steric constraints.

The final Pd–H hydrogen transfer leads to phenol formation. To this regard, DFT calculations carried out by Lercher and co-workers on the catalytic cleavage of benzyl phenyl ether clearly demonstrated that, in the C–O bond cleavage of BPE, the dominant intermediates were benzyl and phenoxy radicals due to the much lower bond dissociation energy (184.3 kJ mol⁻¹) compared to that of phenyl and benzyloxy radicals (332.9 kJ mol⁻¹) and that of the benzyl cation and phenoxy anion (627.7 kJ mol⁻¹) [15].

5.1.4 Catalytic Transfer Hydrogenolysis (CTH) of PPE and DPE

In order to extend the substrate scope, the CTH of 2-phenethylphenylether (PPE) and diphenyl ether (DPE) was finally investigated under the same reaction conditions as those of BPE and results are summarized in Table 5.5.

The reaction of PPE at 240 °C shows a lower conversion (22%) and 100% yield of aromatics (ethyl benzene and phenol). Thus, the experimental data demonstrate again that the Pd/Fe₃O₄ catalyst has a higher selectivity towards the β-O-4 bond cleavage, while the phenyl ring is not involved.

Table 5.5 Transfer hydrogenolysis of aromatic ethers in the presence of the Pd/Fe₃O₄ catalyst. *Conditions:* 0.25 g of catalyst; 60 ml of entry solution – BPE, DPE and PPE 0.1 M; 10 bar N₂; 90 min.

Substrate	Temperature	Conversion	Aromatic selectivity
	[°C]	[%]	[%]
BPE	180	19.7	100
BPE	210	49.4	100
BPE	240	100	100
PPE	240	22	100
DPE	240	< 2	100

On the contrary, under the reaction conditions adopted, DPE was not converted at all. These results can be explained taking into consideration that the 4-O-5 linkage is the most thermally stable bond having a higher bond dissociation energy (314 kJ mol⁻¹) with respect to the β-O-4 (289 kJ mol⁻¹) and the α-O-4 (218 kJ mol⁻¹) C–O bonds [16-18]. Accordingly, the plot of Figure 5.3 shows a linear correlation of the bond strength and the ability of the Pd/Fe₃O₄ catalyst in the CTH of aromatic ethers.

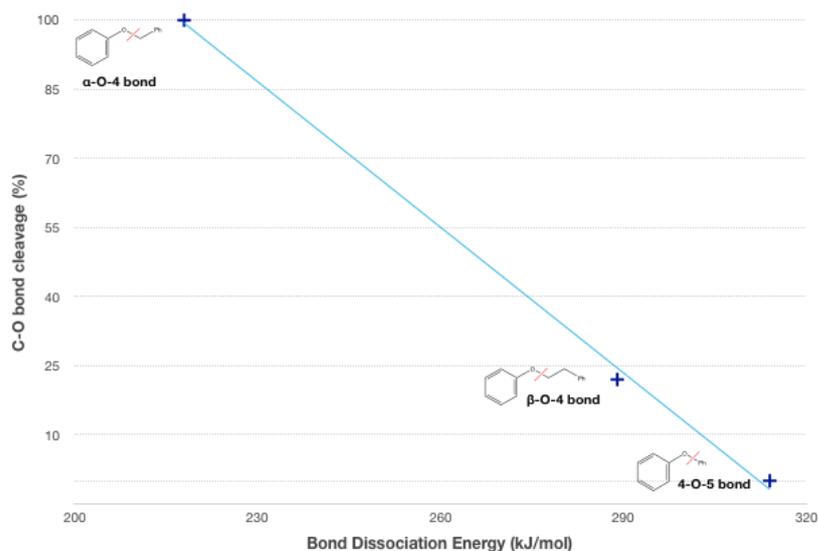


Figure 5.3 C–O cleavage (%) vs bond dissociation energy (kJ/mol) in the CTH of model substrates of α-O-4, β-O-4 and 4-O-5 lignin linkages.

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6

Catalytic valorization of lignin and its derived aromatic ethers promoted by the bimetallic Pd/Co system

6.1 Hydrogenolysis and transfer hydrogenolysis of benzyl phenyl ether (BPE), 2-phenethyl phenyl ether (PPE) and diphenyl ether (DPE)

Table 6.1 reports data referring to the catalytic performance of the bimetallic Pd/Co catalyst in the transfer hydrogenolysis of BPE, compared with those obtained, in the same conditions, with the monometallic Pd/C catalyst.

After 3 hours of reaction, the high BPE conversion at 210°C (88%) and the total conversion (100%) at 240°C evidence the excellent performance of the Pd/Co catalyst. The products distribution pattern changes within the investigated temperature range. Indeed, at the lower temperature (180°C), the only products observed are toluene (Tol) and phenol (Phe). When the temperature increases, phenol is progressively converted into cyclohexanol (CXO) that becomes, at 240°C, the main reaction product together with

toluene. However, this has not to be considered a disfavoured result. It is worth to highlight, in fact, that cyclohexanol is an important feedstock in the industrial chemistry being used as a precursor to nylons, plastics, detergents and insecticides.

Table 6.1. Transfer hydrogenolysis of benzyl phenyl ether (BPE) in the presence of Pd/Co and Pd/C catalysts by using 2-propanol as H-source (Conditions: 0.125 g of catalyst; 40 ml solution of BPE 0.1 M; time: 180 minutes; N₂ pressure: 10 bar; stirring: 500 rpm).

Catalyst	Temperature [%]	Conversion [%]	Chemoselectivity [%]				Aromatic Yield [%]
			TOL	MCX	PHE	CXO	
Pd/Co	240	100	50	-	-	50	50
Pd/C	240	45	50	-	40	10	41
Pd/Co	210	88	50	-	43	7	82
Pd/C	210	18	50	-	50	-	18
Pd/Co	180	30	50	-	50	-	30
Pd/C	180	-	-	-	-	-	-

On the contrary, the commercial Pd/C exhibits a significant lower activity. Indeed, at 210°C the BPE conversion is less than 20% and the maximum is 45% at 240°C, the highest temperature investigated. The modest performance of this monometallic Pd/C catalyst was already observed and attributed to its lower ability to dehydrogenate 2-propanol [1, 2].

Pure metallic cobalt, CoO and Co₃O₄ were also tested within the same temperature range and no BPE conversion was found, clearly indicating that the palladium presence in the catalyst is essential for the C–O bond breaking.

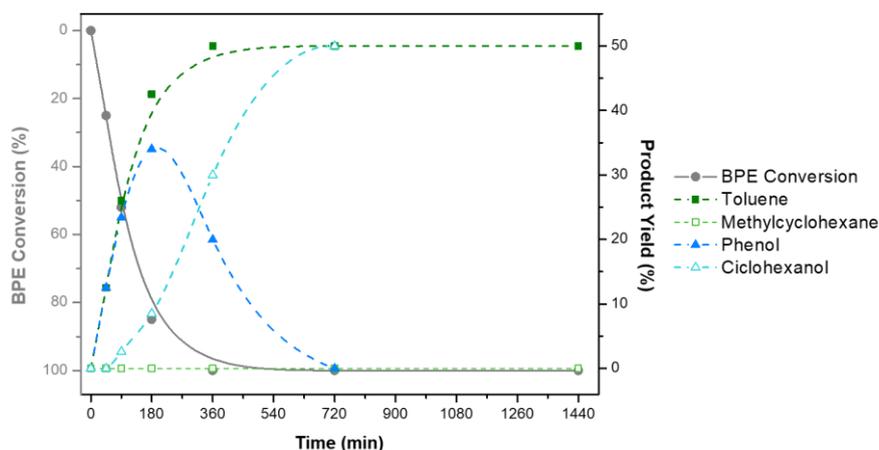


Figure 6.1 Reaction time effect on the BPE conversion (%) and product yields (%) in the CTH at 210 °C. Conditions: 0.125 g of catalyst; 40 ml solution of BPE 0.1 M; N₂ pressure: 10 bar; stirring: 500 rpm.

The lack of any appreciable reactivity, using either Pd/C or Co-based catalysts, confirms that the marked activity shown by the bimetallic Pd/Co catalyst has to be attributed to the strong interaction between palladium and cobalt, as consequence of the preparation method (co-precipitation) in analogy with other reports attaining to glycerol hydrogenolysis [2].

The CTH of BPE, at different reaction times (Figure 6.1.), at 210°C (the best reaction temperature that maximizes aromatic production) was also carried out.

The BPE conversion was completed after 6 h of reaction, and toluene yields progressively increase on increasing reaction times, reaching a maximum value at 360 min. However, no hydrogenation into methylcyclohexane was, in any case, registered. On the other hand, the highest yield of phenol was reached after 180 min and then it progressively decreases because of further hydrogenation to cyclohexanol.

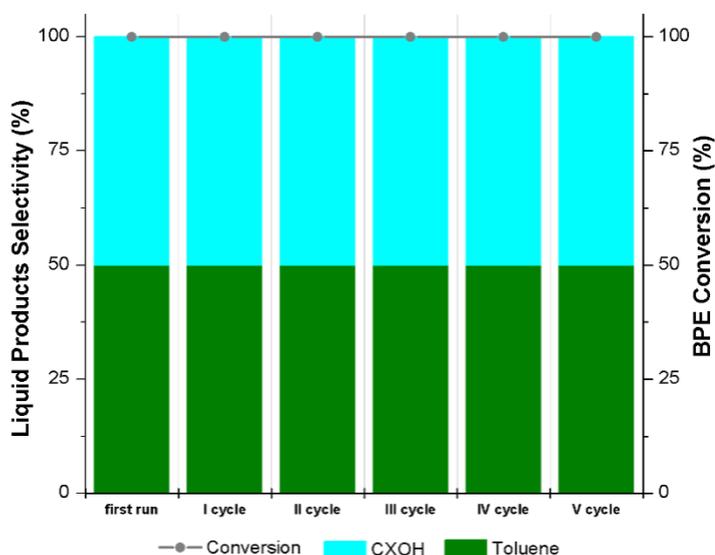


Figure 6.2 Recycling tests relative to the Pd/Co catalyst in the CTH of BPE. *Conditions:* 0.125 g of catalyst; 40 ml solution of BPE 0.1 M; temperature: 240°C; time: 180 minutes; N₂ pressure: 10 bar; stirring: 500 rpm.

The reusability of the Pd/Co catalyst was also evaluated under the harsh reaction condition adopted (240°C for 3 hours). Pd/Co maintains its high activity after six consecutive recycling runs and no changes in product selectivity was found (Figure 6.2). This result clearly highlights the good stability of the catalyst.

The substrate scope was subsequently extended to additional aromatic ethers representative of lignin linkages, namely, PPE and DPE both under CTH conditions as well as under classical hydrogenolysis conditions (Figure 6.3). Catalytic tests show that: (i) improved conversions can be easily achieved in presence of molecular hydrogen and (ii) the cleavage of the C-O bond of PPE and DPE substrates is less efficient due to the higher bond dissociation energies (β -O-4 = 289 kJ/mol and 4-O-5 = 314 kJ/mol) involved [3, 4].

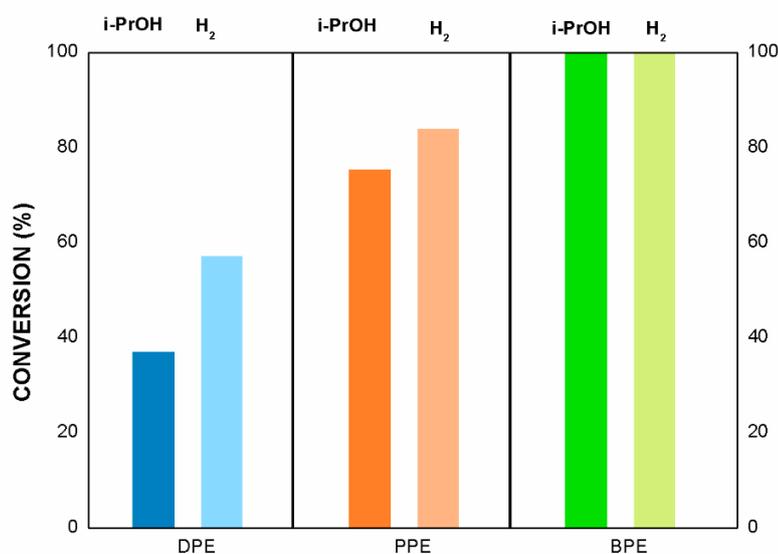


Figure 6.3 . Conversion in the CTH and in the hydrogenolysis of BPE, PPE, and DPE at 240°C. *Conditions:* 0.125 g of catalyst; 40 ml solution of BPE 0.1 M; time: 180 minutes; N₂ or H₂ pressure: 10 bar; stirring: 500 rpm.

6.2 Catalytic Depolymerization of Lignin promoted by the Pd/Co catalyst

Having established the efficiency of Pd/Co catalysts for the cleavage of aromatic ethers that model the α -O-4, β -O-4 and 4-O-5 linkages of lignin, we decided to investigate the depolymerization of organosolv lignin samples isolated from the olive tree pruning.

The depolymerization of lignin was conducted in the presence of the Pd/Co catalyst under CTH conditions (1 g of lignin; 0.400 g of catalyst; 40 ml solution of 2-PrOH; temperature: 300°C; time: 12 h; N₂ pressure: 50 bar; stirring: 500 rpm). At the end of the reaction, more than 95% weight of the starting lignin was recovered as a thick oil product.

Analysis of the resulting samples were carried out by gel permeation chromatography (GPC) and NMR analysis.

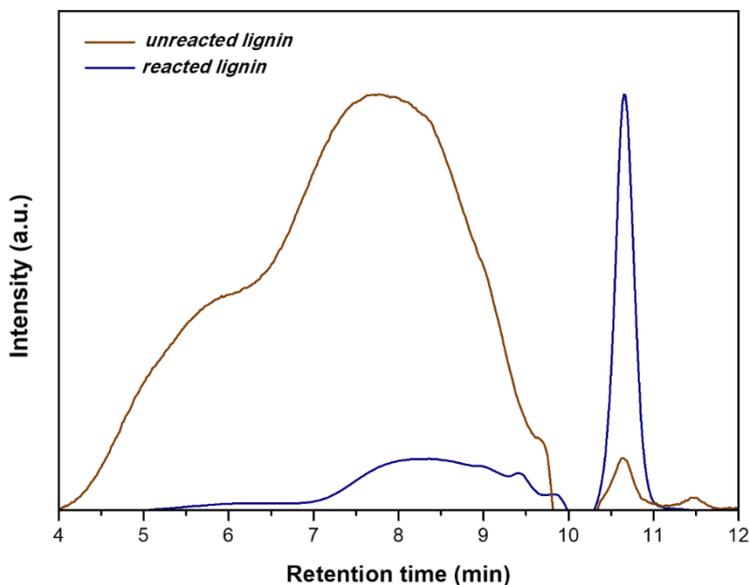


Figure 6.4 GPC diagrams of unreacted organosolv lignin (brown line) and product mixture from the CTH reaction (blue line).

Gel Permeation Chromatography (GPC) analysis showed that the average molecular weight (Mw) decreased from 6729 attaining to the initial lignin sample to 3879 relative to the oil isolated after the CTH reaction. The occurred lignin depolymerization is also evident from GPC diagrams of the organosolv lignin (brown line) and the product mixture from the CTH reaction (blue line) reported in Figure 6.4 where, in the latter case, it is evident the decrease of the broad peak centered at about 8 min together with a simultaneous increase of the peak centered at 10.65 min, indicating the formation of monomeric and dimeric aromatic products [5-6].

2D-HSQC analysis confirms that organosolv lignin undergoes depolymerization (Figure 6.5). In the unreacted organosolv lignin, in the aromatic region, signals from p-hydroxyphenyl (P), guaiacyl (G), syringyl (S), guaiacyl' (G') and syringyl' (S') units were clearly observed, which are generally identified in the hardwood lignin [7-11].

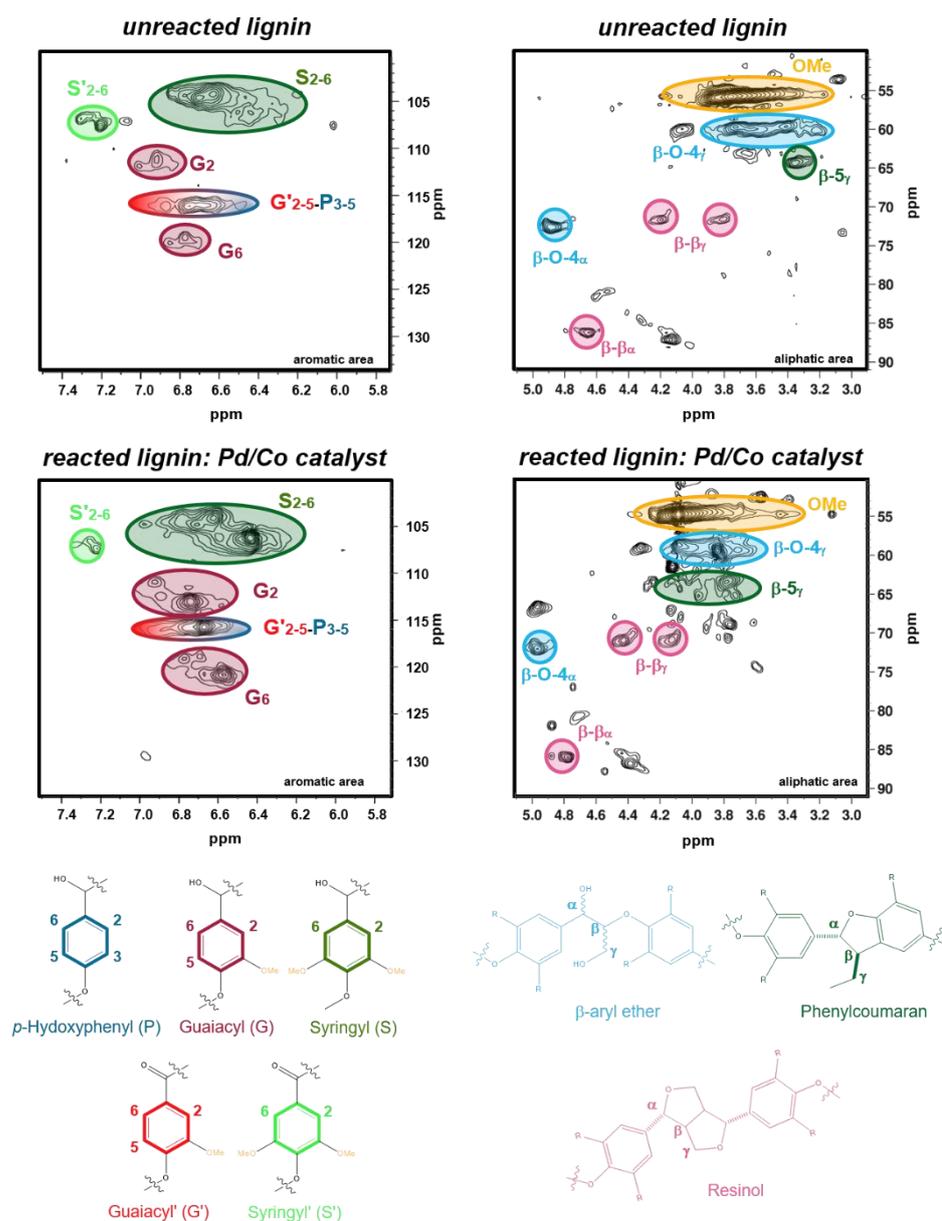


Figure 6.5 Images of 2D-HSQC NMR analysis: assignment of linkages and monomeric units of unreacted (up) and reacted (down) olive tree pruning lignin

Accordingly, in the aliphatic region, the β -O-4, β - β and β -5 are noticed as the predominant lignin-lignin intralinkages.

After the hydrogenolysis reaction in the presence of the Pd/Co catalyst, the strength of signals corresponding to the β -O-4 linkages in the aliphatic area of the reacted lignin is much less intense than that of the unreacted material. At the

same time, the increase of 2D-HSQC signals in the aromatic area of CTH products is indicative of formation of guaiacol and syngol monomeric units. Similarly, an increase of signals from secondary alkyl protons of β -5 linkages (crosspeak between 3.6-4.2 ppm in ^1H and 65 ppm in ^{13}C in the top spectrum) was observed.

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7

Catalytic valorization of lignin and its derived aromatic ethers promoted by the bimetallic Pd/Ni system

7.1 Catalytic Transfer Hydrogenolysis (CTH) reactions

Primarily the attention was focused on the CTH of DPE that has a dissociation C–O bond energy of 314 kJ/mol, the strongest structural link in lignin that, to be broken, generally requires harsh reaction conditions. The catalytic performances of the bimetallic Pd/Ni catalyst in the transfer hydrogenolysis of DPE are reported in Table 7.1.

The reaction proceeds appreciably at 180 °C (39% conversion in 90 min). In addition to BEN and PHE, CXO is also obtained as reaction product (14% selectivity). DPE conversion progressively rises (from 65% at 210 °C to 96% at 240 °C) on increasing the reaction temperature.

Table 7.1 Transfer hydrogenolysis of benzyl phenyl ether promoted by Pd/Co catalyst. Conditions: 0.25 g of catalyst; 60 ml of entry solution – DPE 0.1 M; 10 bar N₂; 90 min.

Catalyst	Temperature [%]	Conversion [%]	Chemoselectivity [%]				Aromatic Yield [%]
			BEN	CHX	PHE	CXO	
Pd/Ni	240	96,1	44	5	4	46	47
Ni	240	79,4	44	6	4	46	37
Pd/Ni	210	64,5	49	1	30	20	50
Ni	210	43,3	48	2	18	32	29
Pd/Ni	180	39,3	50	-	36	14	33
Ni	180	10,7	50	-	29	21	8

The highest production of aromatic products could be observed at 210 °C where a selectivity of 48% and 30% to BEN and PHE, respectively, was measured. At 240 °C, a mixture of BEN (45%), CHX (6%), PHE (4%), and CXO (46%) was obtained.

With 210 °C, identified as the optimum reaction temperature to maximize the aromatic production, the CTH of DPE was also investigated at different reaction times (Figure 7.1). As the reaction proceeds, in the presence of Pd/Ni, the BEN yield progressively increases, and only after 360 min, a discrete amount of CHX is registered. Comparatively, phenol reaches the highest yield value (19%, 90 min), progressively decreasing because of further hydrogenation into cyclohexanol.

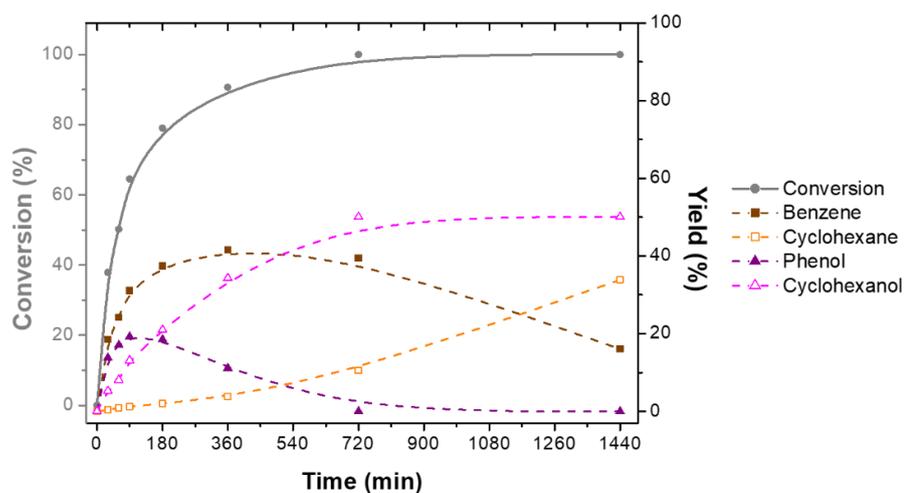


Figure 7.1 Reaction time effect on the BPE conversion (%) and liquid products selectivity (%) in the CTH at 210 °C.

A control experiment on the CTH of phenol (210 °C, 10 bar N₂, 90 min) gives a 97% yield of cyclohexanol under identical reaction conditions (see below). The larger phenol hydrogenation tendency observed, with respect to that of benzene, is in good agreement with previous literature reports[1, 2]. Analogous results were obtained at 180 and 240 °C.

The reusability of Pd/Ni, based on consecutive recycling tests at 210 °C for 90 min, was subsequently evaluated using the DPE conversion as model reaction. Pd/Ni maintains its activity after eight consecutive runs and only slight changes in the product selectivity were found, highlighting the good stability of the catalyst (Figure 7.2).

Pd/Ni could also be magnetically recoverable and directly recycled (simple washing with 2-propanol is necessary) for the next reaction run (Figure 7.2).

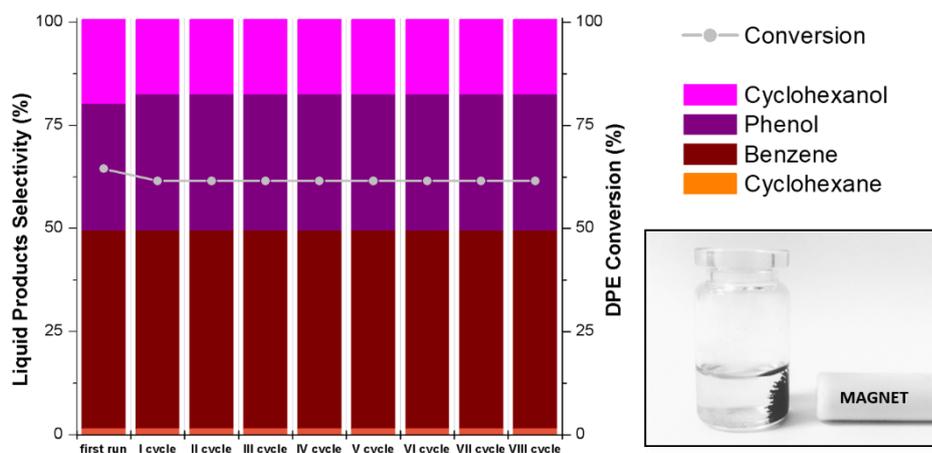


Figure 7.2 Recycle of the Pd/Ni catalyst in the transfer hydrogenolysis of BPE (210°C; 180 min; 0,125 g catalyst; 40ml entry solution 0.1 M; 10 bar N₂ pressure).

At all reaction temperatures investigated, the monometallic Ni catalyst shows a markedly reduced activity. DPE conversion was ca. 10% at 180 °C and reaches a maximum value of 79% at 240 °C.

At the same time, a much higher tendency toward aromatic ring hydrogenation is always registered. In order to exclude the possibility that the activity of Pd/Ni may arise from the simple sum of both the monometallic Ni and Pd species, additional CTH reactions of DPE were carried out using Pd/C or unsupported metal palladium (resulting from the in situ reduction of PdO). In both cases, the molar amount of palladium was carefully checked to be equal to that of Pd/Ni catalysts used in all catalytic experiments (5.64 mol × 10⁻³ mol of Pd). The quantity of products observed at all investigated temperatures was indeed negligible, confirming that only Pd/Ni bimetallic species positively promote the CTH reaction of aromatic ethers.

7.2 Hydrogenolysis reactions

The DPE C–O bond hydrogenolysis was also promoted using molecular hydrogen at 210 °C (Table 7.2), and an increase in the production of aromatic ring hydrogenation derivatives (CXO and CHX) was noticed. On increasing the initial H₂ pressure, a slight decrease in DPE conversion could be observed although the aromatic yield remains above 40% (53%, 48%, and 41% at 10, 20, and 40 bar of the initial H₂ pressure, respectively).

The inhibitory effect of hydrogen pressure on hydrogenolysis reactions was already reported and previously attributed to a hydrogen/substrate competitive adsorption on the catalyst surface [3, 4].

Table 7.2 Hydrogenolysis of DPE promoted by the Pd/Ni catalyst by using molecular hydrogen as H-source. (Conditions: 0.2 g of catalyst, 60 ml solution of diphenyl ether (0.1 M), solvent: isopropanol; H₂ pressure: 10 bar; stirring: 500 rpm; Temperature: 210°C).

Pressure [min]	Conversion [%]	Chemoselectivity [%]				Aromatic Yield [%]
		BEN	CHX	PHE	CXO	
40	65	42	8	21	29	41
20	71	44	6	22	28	47
10	73	46	4	27	23	53

7.3 CTH of Diphenyl ether in presence of water and water/2-propanol mixture as H-donor

DPE was efficiently reduced also using a water/2-propanol mixture (50 wt %) with very similar conversions and chemoselectivities under both CTH and hydrogenolysis conditions (Table 7.3). Unexpectedly, no DPE conversion was obtained by using only water as solvent suggesting that the Pd/Ni catalyst is not able to promote both hydrogenolysis and/or hydrolysis of the etheric C–O bond in pure water.

Table 7.3 Hydrogenolysis and Transfer hydrogenolysis of DPE promoted by Ni-based catalysts by using water and a water/2-propanol mixture (50% wt) as solvent. Condition: 0.2 g of catalyst, 60 ml solution of diphenyl ether (4% wt), H₂ or N₂ pressure: 10 bar; stirring: 500 rpm.

Solvent	Condition	Conversion [%]	Aromatic Yield [%]
H ₂ O	hydrogenolysis	-	-
H ₂ O	CTH	-	-
H ₂ O/i-PrOH	hydrogenolysis	63	45
H ₂ O/ i-PrOH	CTH	57	46

These results are in contrast with those included in a recent report which discloses the ability of palladium catalysts in the hydrolytic cleavage of aromatic ethers [59].

7.4 Catalytic Hydrogenolysis and Transfer Hydrogenolysis (CTH) of BPE and PPE

Having demonstrated the efficiency of Pd/Ni in the hydrogenolysis and the CTH of diphenyl ether, the substrate scope was subsequently extended to the other aromatic ethers representative of lignin linkages, namely, PPE and BPE. CTH catalytic tests, carried out at 210 °C, show that improved conversions can be easily achieved because of lower dissociation energies for C–O bonds involved (β -O-4 = 289 kJ/mol and α -O-4 = 218 kJ/mol) with respect to that of DPE (4-O-5 = 314 kJ/mol).

In particular, BPE shows a conversion of 98%, with an aromatic yield of 97% whereas, in the case of PPE, a lower conversion (conversion, 67%; aromatic yield, 60%) was obtained.

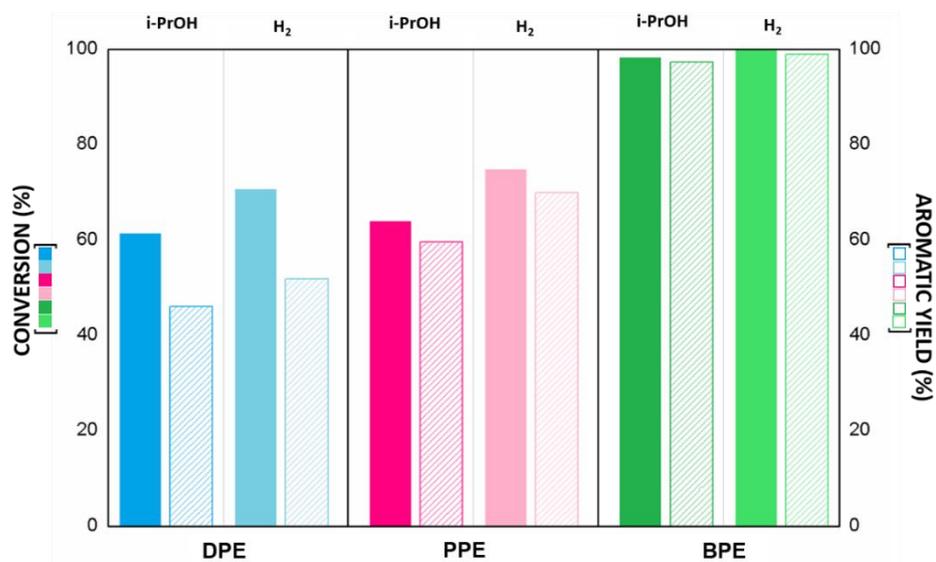


Figure 7.3. Conversion (%) and aromatic yield (%) in the CTH and in the hydrogenolysis of benzyl phenyl ether (BPE), 2-phenethyl phenyl ether (PPE) and diphenyl ether (DPE). Conditions: 0.2 g of catalyst, 60 ml solution of diphenyl ether (4% wt), solvent: isopropanol; N₂/H₂ pressure: 10 bar; stirring: 500 rpm; Temperature: 210°C.

For comparison, BPE and PPE were also tested using H₂ at an initial pressure of 10 bar. Under hydrogenolysis conditions, BPE is fully converted with an outstanding selectivity to aromatics (>99%) while PPE conversion slightly overcomes 75% with a high aromatic yield (70%).

The very high aromatic selectivity registered in the CTH and hydrogenolysis of BPE and PPE suggested to extend the investigation to the hydrogenation of phenol in the presence and in absence of molecular hydrogen. Catalytic tests at 210 °C clearly show:

- I. that the hydrogenation of phenol is faster than the hydrogenolysis of DPE, PPE, and BPE both under CTH as well as under hydrogenolysis conditions;
- II. that the reaction proceeds through the intermediate cyclohexanone using 2-propanol; and

- III. that very low conversion into benzene is observed, in good agreement with other literature reports [5, 6].

These results, analyzed together with those relative to aromatic ethers, imply that the hydrogenation process of phenol is very sensitive to the presence of other chemical species on the reaction system.

Therefore, we carried out competitive catalytic hydrogenation reactions of phenol in mixture with benzene, toluene, and ethylbenzene added in equimolar feed composition at 210 °C under CTH conditions to mimic the reduction of phenol formed upon C–O bond cleavage. Results are reported in Figure 7.4 and clearly show that hydrogenation of phenol progressively decreases in the presence of benzene (89%), toluene (72%), and ethylbenzene (64%).

Therefore, the addition in the reaction system of another aromatic molecule affords a 2-fold consequence on the hydrogenation of phenol: (i) a lower production of cyclohexanol and (ii) a decrease of aromatic ring saturation as more as the arene derivative is substituted.

The only possible conclusion is that a competitive adsorption between phenol and added aromatic hydrocarbons occurs on catalytic sites. The latter are more easily chemisorbed on the Pd/Ni surface with respect to phenol as the inductive effect of the substituent group at the ring increases (ethylbenzene > toluene > benzene).

An analogous interpretation was already reported on the coordination chemistry of benzene and toluene on nickel (111), (110), and (100) surfaces [7].

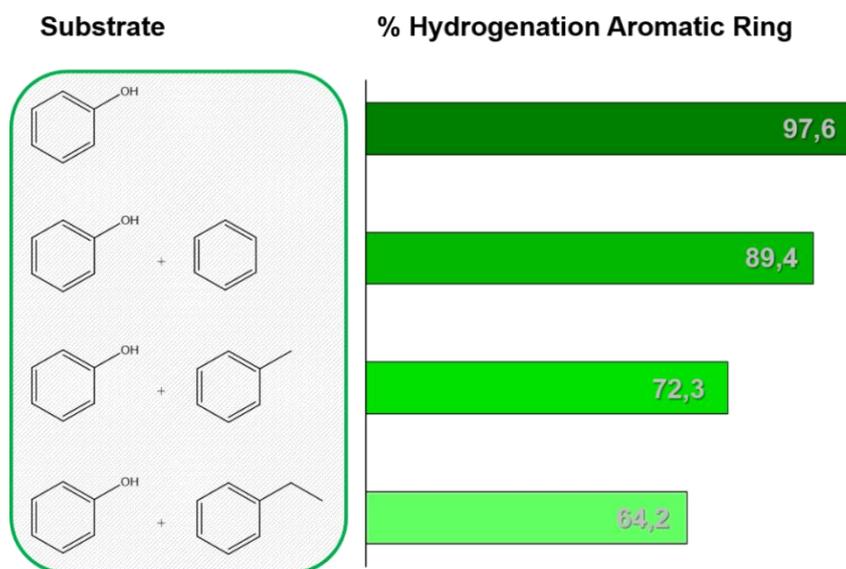


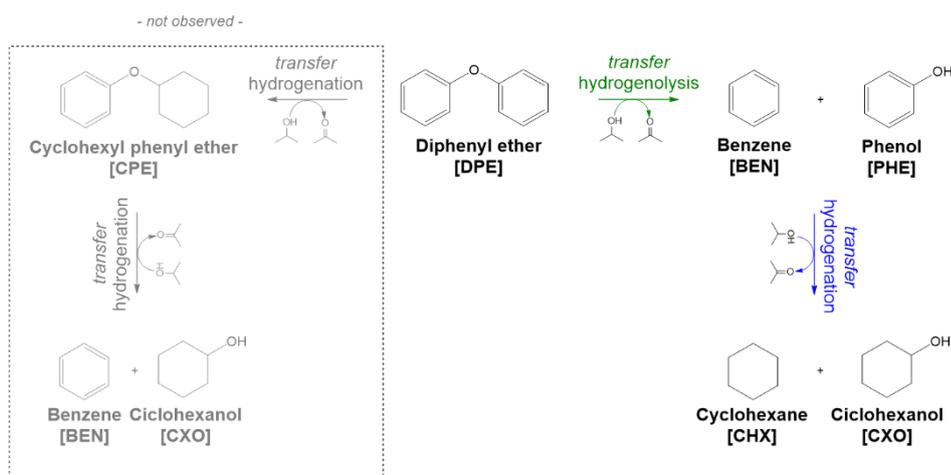
Figure 7.4 Competitive catalytic hydrogenation of phenol in mixture with benzene, toluene, and ethylbenzene at an equimolar feed composition at 210 °C under CTH conditions.

As far as we know, this concept - supported by experimental evidence - has been for the first time extended to the hydrogenolysis/hydrogenation of aromatic ethers.

7.5 Elucidating the CTH Reaction Pathway

In principle, DPE catalytic transfer hydrogenation may occur via alternative pathways (Scheme 7.1): (i) direct C–O bond cleavage, affording phenol (PHE) and benzene (BEN) as primary products that may be further hydrogenated, respectively, into cyclohexane (CHX) and cyclohexanol (CXO) or (ii) a previous hydrogenation of DPE into cyclohexyl phenyl ether (CPE) that, in a successive step, may undergo hydrogenolysis allowing the formation of BEN and CXO.

In all experiments, cyclohexyl phenyl ether (CPE) was never detected suggesting that CXO is formed from PHE hydrogenation. For a corroboration of this hypothesis, CPE was allowed to react under the same reaction conditions adopted for DPE in a reference experiment.



Scheme 7.1. Possible reaction pathways for the C-O bond cleavage of diphenyl ether under CTH conditions.

No substrate conversion was observed confirming that the first step, in the transfer hydrogenolysis of DPE, is the direct cleavage of the C-O bond.

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8

Final Conclusions

The three years of my PhD work, described in the present Thesis, have been devoted to the investigation of the performance of co-precipitated bimetallic Pd based catalysts for the conversion of lignin-derivable molecules, starting from model aromatic ethers, such as Benzyl Phenyl Ether (BPE), 2-Phenethyl Phenyl Ether (PPE) and Diphenyl Ether (DPE), and, finally, organosolv lignin.

The physico-chemical and the structural properties of the co-precipitated Pd/Fe₃O₄, Pd/Co and Pd/Ni catalysts have been characterized through XRD, SEM, TEM, H₂-TPR, XPS and EXAFS measurements. These physico-chemical techniques highlight the presence of well dispersed palladium nanoparticles and reveal the existence of a strong metal-support interaction (in the case of the Pd/Fe₃O₄ catalysts) and alloys (in the case of Pd/Co and Pd/Ni catalysts) that enhance the ability of coprecipitated systems in the C-O bond cleavage of aromatic ethers.

All catalytic tests were conducted under transfer hydrogenolysis conditions using 2-propanol as H-donor/solvent. The Pd/Fe₃O₄ catalyst is able to cleave the C-O bond of benzyl phenyl ether (BPE) under CTH conditions and, at the same time, to avoid parallel hydrogenation reactions of the aromatic ring, being one of the most selective

heterogeneous catalysts in the production of arene derivatives. The experimental evidence shows that the direct hydrogen transfer from the α -H of the donor solvent to BPE occurs in a unique process.

The bimetallic Pd/Co catalyst, prepared by the coprecipitation technique, is able to effectively cleave the C–O bond of benzyl phenyl ether that, after 3 hours at 240°C, is selectively converted into toluene and cyclohexanol. Six consecutive recycling tests in the transfer hydrogenolysis of BPE proved the good stability of the Pd/Co catalyst that can be easily recoverable magnetically.

On the other hand, the CTH of the ethereal C–O bond of 2-phenethyl phenyl ether and diphenyl ether, in presence of both Pd/Fe₃O₄ and Pd/Co catalysts, were found to be less efficient due to the higher bond dissociation energies involved.

The etheric C–O bond of all investigated lignin derived aromatic ethers was efficiently cleaved also by the bimetallic Pd/Ni catalyst that can be efficiently used up to eight consecutive recycling tests and that can be easily recoverable magnetically from the reaction medium. The catalytic tests clearly evidence that, in presence of the Pd/Ni catalyst, cyclohexyl phenyl ether (CPE) is not a reaction intermediate revealing that the first step in the transfer hydrogenolysis of DPE is the direct cleavage of the C–O bond. Noteworthy, competitive catalytic hydrogenation reactions of phenol in mixture with benzene, toluene and ethylbenzene demonstrate that, the production of aromatics in the transfer hydrogenolysis of DPE, PPE and PPE is deeply influenced by the nature of the aryl groups that form the aromatic ether

structure with a production of cyclohexanol that decreases as more as the arene derivative is substituted.

Preliminary results on the lignin transfer hydrogenolysis were also obtained, on using the Pd/Co catalyst, and they encourage the use of our catalysts on the direct CTH of the lignin as an industrial tool for converting biomasses to resources.

Other activities

Scientific production

Reverse chronological order

T. Tabanelli, **E. Paone**, P. B. Vázquez, R. Pietropaolo, F. Cavani, F. Mauriello

Comparing batch and continuous gas-flow conditions in the transfer hydrogenation of methyl and ethyl levulinate promoted by tetragonal ZrO₂ catalyst.

ACS Sustainable Chemistry & Engineering, 2019, *Manuscript submitted*

F. Mauriello, H. Ariga-Miwa, **E. Paone**, R. Pietropaolo, S. Takakusagi, K. Asakura

Transfer hydrogenolysis of aromatic ethers promoted by the bimetallic Pd/Co catalyst.

Catalysis Today, 2019, *Manuscript submitted*

A. Malara, **E. Paone**, P. Frontera, L. Bonaccorsi, G. Panzera, F. Mauriello

Sustainable exploitation of coffee silverskin in water remediation. Sustainability, 2018, 10(10), 3547.

C. Espro, B. Gumina, T. Szumelda, **E. Paone**, F. Mauriello
Catalytic transfer hydrogenolysis as an effective tool for the
reductive upgrading of cellulose, hemicellulose, lignin and their
derived platform molecules.
Catalysts, 2018, 8(8), 313.

F. Mauriello, **E. Paone**, R. Pietropaolo, A.M. Balu, R. Luque
Catalytic transfer hydrogenolysis of lignin derived aromatic ethers
promoted by bimetallic Pd/Ni systems.
ACS Sustainable Chemistry & Engineering, 2018, 6(7), 9269-9276.

P. S. Calabrò, **E. Paone**, D. Komilis
Strategies for the sustainable management of orange peel waste
through anaerobic digestion.
Journal of Environmental Management, 2018, 212, 462-468.

C. Espro, B. Gumina, **E. Paone**, F. Mauriello
Upgrading lignocellulosic biomasses: hydrogenolysis of platform
derived molecules promoted by heterogeneous Pd-Fe catalysts.
Catalysts, 2017, 7(3), 78.

E. Paone, C. Espro, R. Pietropaolo, F. Mauriello
Selective arene production from transfer hydrogenolysis of benzyl
phenyl ether promoted by a co-precipitated Pd/Fe₃O₄ catalyst.
Catalysis Science & Technology, 2016, 6(22), 7937-7941.

Communication

Sustainable Exploitation of Coffee Silverskin in Water Remediation

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Abstract: Coffee silverskin (CS), the main solid waste produced from the coffee industry, has efficiently been used as adsorbent material to remove potential toxic metals (PTMs). In order to assess its suitability in water remediation, kinetic adsorption experiments of Cu^{2+} , Zn^{2+} , and Ni^{2+} ions from wastewater were carried out and the adsorption performance of the waste material was compared with that of another well-known waste from coffee industry, spent coffee grounds (SCG). By using CS as sorbent material, ion removal follows the order $\text{Cu}^{2+} > \text{Zn}^{2+} > \text{Ni}^{2+}$ with the adsorption equilibrium occurring after about 20 min. The adsorption efficiency of Ni^{2+} ions is the same for both investigated materials, while Cu^{2+} and Zn^{2+} ions are removed to a lesser extent by using CS. Equilibrium-adsorption data were analyzed using two different isotherm models (Langmuir and Freundlich), demonstrating that monolayer-type adsorption occurs on both CS and SCG surfaces. The overall results support the use of coffee silverskin as a new inexpensive adsorbent material for PTMs from wastewater.

Keywords: potential toxic metals; coffee waste; coffee silverskin; spent coffee grounds; metal adsorption; remediation; Langmuir and Freundlich isotherm models; wastewater

1. Introduction

In the past few years, in the framework of environmental sustainability research, numerous attempts on the reuse and valorization of coffee byproducts and coffee wastewater have been developed [1].

Coffee is the most important food commodity worldwide, being the second-most traded product after oil [2]. Because of this extended market, the coffee industry produces huge volumes of waste. In fact, each stage of the coffee production process (i.e., coffee-cherries processing, dried-beans milling, green-coffee-beans roasting), as well as coffee consumption, each year produces a large volume of biowaste, which contributes to environmental pollution [3]. Among this biowaste, residues with coffee silverskin (CS) and spent coffee grounds (SCG) are the most significantly produced. Since sustainability development has to be prioritized, research devoted to valorizing and reusing this kind of waste should be strongly encouraged in a strategy for the treatment of end-of-life materials [4].

CS is a thin integument of the outer layer of green coffee beans that comes off during the roasting process [5]. Moreover, it is generally produced in high volumes, takes fire very easily, and its disposal requires the use of energy for the necessary compaction process.

SCG are also a well-known residual material obtained from instant-coffee preparation or coffee brewing. SCG are a residue obtained during the treatment of raw coffee powder with hot

Review

Catalytic Transfer Hydrogenolysis as an Effective Tool for the Reductive Upgrading of Cellulose, Hemicellulose, Lignin, and Their Derived Molecules

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Abstract: Lignocellulosic biomasses have a tremendous potential to cover the future demand of bio-based chemicals and materials, breaking down our historical dependence on petroleum resources. The development of green chemical technologies, together with the appropriate eco-politics, can make a decisive contribution to a cheap and effective conversion of lignocellulosic feedstocks into sustainable and renewable chemical building blocks. In this regard, the use of an indirect H-source for reducing the oxygen content in lignocellulosic biomasses and in their derived platform molecules is receiving increasing attention. In this contribution we highlight recent advances in the transfer hydrogenolysis of cellulose, hemicellulose, lignin, and of their derived model molecules promoted by heterogeneous catalysts for the sustainable production of biofuels and biochemicals.

Keywords: lignocellulosic biomasses; H-donor molecules; hydrogenolysis; catalytic transfer hydrogenolysis reactions; heterogeneous catalysis; cellulose; hemicellulose; lignin; glycerol; polyols; furfural; levulinic acid; aromatic ethers

1. Introduction

The hegemony of fossil resources is declining by now. In the last few decades, industrial chemistry has accepted the challenge for the sustainable production of chemicals and energy by using renewable biomasses as starting supplies [1]. Moreover, the changes in consumer attitudes towards “green” products, as well as government initiatives for sustainable development programs and regulations, are surely the key driving factors for the development of the bio-based chemical industries and refineries [2–6].

While many criticisms have been raised towards the first generation of bio-energies and biofuels since they are in direct competition with human and animal food, reducing the land availability [7], we have recently achieved significant progress in the production of chemical building blocks and intermediates from lignocellulosic wastes and residues [8–20]. This is because their use in the chemical industry presents several advantages including: (i) the production of less toxic by-products and lower environmental risks, (ii) the reduction of CO₂ emissions, (iii) a minor dependence on fossil resources and/or foreign commodities, and (iv) the use of indigenous raw materials that can add value in many agriculture products or processes.

Catalytic Transfer Hydrogenolysis of Lignin-Derived Aromatic Ethers Promoted by Bimetallic Pd/Ni Systems

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Supporting Information

ABSTRACT: Catalytic transfer hydrogenolysis (CTH) of diphenyl ether (DPE), 2-phenethyl phenyl ether (PPE), and benzyl phenyl ether (BPE)—as model molecules of α -O-4 and β -O-4 as well as 4-O-5 lignin linkages—promoted by bimetallic Pd/Ni systems is reported. Pd/Ni (Pd loading of 3 wt %) catalysts were synthesized by using a simple and economic coprecipitation technique, and its detailed physicochemical characterization was performed by means of H₂-TPR, XRD, TEM, and XPS analysis. In the presence of palladium as cometal, an almost complete conversion of DPE was reached after 90 min at a temperature of 240 °C while BPE and PPE C–O bond breaking could be achieved at milder reaction conditions. Pd/Ni bimetallic systems can be magnetically recovered and efficiently used up to eight consecutive recycling tests in the transfer hydrogenolysis of DPE. The investigated substrates were also tested using analogous Ni monometallic systems. Palladium as cometal present in the catalysts was proven to increase the C–O bond cleavage rates and decrease aromatic ring hydrogenation selectivity. The catalytic tests on all possible reaction intermediates clearly show that the hydrogenolysis cleavage in etheric C–O bond breaking was the rate-determining step under CTH conditions, while hydrogenations only take place in a successive step. Moreover, it has been demonstrated that the hydrogenation of phenol formed from CTH depends on the type of aryl groups that form the aromatic ether structure.

KEYWORDS: Catalytic transfer hydrogenolysis, Aromatic ethers, Heterogeneous catalysis, Nickel, Palladium, Bimetallic catalysts



INTRODUCTION

One of the major challenges of modern refineries relates to the synthesis of biochemicals and biomaterials from nonedible lignocellulosic feedstocks.^{1–4} Lignin, the most abundant natural phenolic biopolymer, is of particular interest for chemical industries since it may allow a future sustainable production of aromatic compounds and intermediates.^{5–8} In the past several years, many strategies have been proposed for lignin depolymerization into readily available aromatic compounds.^{3,9,10} Since the lignin substructure is characterized by large amounts of etheric bonds, catalytic hydrogenolysis has received strong attention, allowing C–O bond breaking by adding molecular hydrogen.¹¹ However, the hydrogenolysis of lignin generally requires harsh reaction conditions due to the high dissociation energies involved in C–O bond cleavage.^{12,13} Furthermore, the use of high-pressure molecular hydrogen leads to undesired aromatic ring hydrogenated products, thus decreasing the process efficiency and lowering the degree of lignin depolymerization (fully saturated products are less susceptible to a further hydrogenolysis process). As a

consequence, the preparation of catalysts able to selectively cleave the C–O bond in the presence of aromatic functionalities together with a deep insight on the basic chemistry of aromatic ethers remains challenging in the aim to develop selective chemical processes to produce aromatics from lignin.

Because of the good availability and the competitive market price of nickel precursors with respect to other transition metals, significant interest was mainly devoted to address the design of homogeneous and heterogeneous Ni-based catalysts for hydrogenolysis of aromatic ethers.¹⁴ While homogeneous nickel catalysts were found highly efficient in reductive C–O bond cleavage of aryl-alkyl ethers and diaryl ethers under mild reaction conditions,^{15,16} their application in lignin depolymerization has been partially limited for their high separation costs, reusability, and handling. At the same time, in the

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Research article

Strategies for the sustainable management of orange peel waste through anaerobic digestion

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ABSTRACT

The processing of oranges is a major industry worldwide and leads to the production of large amounts of orange peel waste (OPW). Energy production through anaerobic digestion of OPW is a promising option; however, the high content of essential oil, mainly composed of *D*-limonene, a well-known antioxidant, can cause the inhibition of the biological activity. In this paper, different pretreatment methods were tested (e.g. ensiling, aeration, thermal and alkaline treatments) to optimize the anaerobic digestion of OPW focusing on *D*-limonene removal. The raw and pretreated substrates were characterized and their biochemical methane production was measured. The results demonstrated the ability of some of the treatments to reduce *D*-limonene content up to 80%. A relatively high biomethane potential production of OPW (up to about 500 NmL CH₄ g⁻¹ VS) was measured. The importance of the acclimation of inoculum and the risk connected to the accumulation of inhibiting substances in the reactor is discussed.

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1. Introduction

Orange juice is an important agro-industrial product at global level (production of 1.6 Tg was estimated during harvesting season 2015–2016 according to the United States Department of Agriculture (2016)). Its production leads to the generation of a large amount of orange peel waste (OPW) that represents about 50–60% (wb) of the processed fruit (Martín et al., 2010). OPW includes rotten/discarded fruits, peel, seeds and membrane residues (Wilkins et al., 2007) and contains water (75–85% wb), simple sugars (glucose, fructose, sucrose; 6–8% db), polysaccharides (pectin, cellulose and hemicellulose; 1.5–3% db). It is characterized by a very low pH (3–5) and a significant presence of essential oil (EO), which is composed mainly by *D*-limonene (83–97%) (Bicas et al., 2008).

OPW presents a very high potential for bio-refining. Several valorisation routes have been proposed (e.g. production of fertilizers, pectin, ethanol, EO, chemicals, cattle feed, absorbent material (Ángel Siles López et al., Ángel Siles López et al., 2010; Boukroufa et al., 2015; Farhat et al., 2011; Tripodo et al., 2004; Ángel Siles López et al., 2010; Boukroufa et al., 2015; Farhat et al.,

2011; Tripodo et al., 2004). Another possible valorisation option could be via the use of solid state fermentation (SSF) that until now has never been applied to OPW but has fully demonstrated its valorisation potential on other organic substrates (Ballardo et al., 2016; El-Bakry et al., 2015; Jiménez-Peñalver et al., 2016). Unfortunately, some of the aforementioned technologies are not mature or economically sustainable to be implemented in full scale and, therefore, OPW is typically used as a fodder after ensiling or drying or it is landfilled uncontrollably near the production sites (Ángel Siles López et al., Ángel Siles López et al., 2010; Tripodo et al., 2004; Ángel Siles López et al., 2010; Tripodo et al., 2004).

Energy production through anaerobic digestion is a promising and sustainable option for OPW; however, the high content of EO which mainly comprises *D*-limonene, a well-known antioxidant, can cause the inhibition of biomass activity (Forgács et al., 2012; Martín et al., 2010; Ruiz and Flotats, 2014). There are two possible options to overcome this limitation:

- The codigestion of OPW (fresh or ensiled) with other substrates (Anjum et al., 2017; Forgács et al., 2012; Martín et al., 2013) to dilute the *D*-limonene load;
- The OPW pretreatment to reduce the *D*-limonene content (Martín et al., 2010; Ruiz et al., 2016).

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Review

Upgrading Lignocellulosic Biomasses: Hydrogenolysis of Platform Derived Molecules Promoted by Heterogeneous Pd-Fe Catalysts

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Abstract: This review provides an overview of heterogeneous bimetallic Pd-Fe catalysts in the C–C and C–O cleavage of platform molecules such as C2–C6 polyols, furfural, phenol derivatives and aromatic ethers that are all easily obtainable from renewable cellulose, hemicellulose and lignin (the major components of lignocellulosic biomasses). The interaction between palladium and iron affords bimetallic Pd-Fe sites (ensemble or alloy) that were found to be very active in several sustainable reactions including hydrogenolysis, catalytic transfer hydrogenolysis (CTH) and aqueous phase reforming (APR) that will be highlighted. This contribution concentrates also on the different synthetic strategies (incipient wetness impregnation, deposition-precipitation, co-precipitation) adopted for the preparation of heterogeneous Pd-Fe systems as well as on the main characterization techniques used (XRD, TEM, H₂-TPR, XPS and EXAFS) in order to elucidate the key factors that influence the unique catalytic performances observed.

Keywords: heterogeneous catalysis; palladium; iron; iron oxides; bimetallic catalysts; cellulose; polyols; hemicellulose; furfural; lignin; phenol derivatives; aromatic ethers; hydrogenolysis; hydrodeoxygenation (HDO); catalytic transfer hydrogenolysis (CTH); aqueous phase reforming (APR)

1. Introduction

Modern chemical industry is facing the big challenge of overcoming its historical dependence on fossil resources by reconciling the economic recovery with the protection of environment and the reduction of greenhouse gas emissions. At the 21st United Nations Climate Change Conference (COP21), 195 nations agreed on a global action plan aimed to limit the global warming below 2 °C above pre-industrial levels. The “Paris Agreement” comes into force on the 4th November 2016 and is expected to be a new course in the global climate effort [1].

To achieve this ambitious goal, several countries are releasing new green economy strategies. USA have launched the “National Bioeconomy Blueprint Program” addressing five strategic objectives able to generate economic growth and to meet societal needs [2]. Accordingly, the EU has set a “Bioeconomy Strategy and Action Plan” [3–5] identifying, under the Framework Programme for Research and Innovation in Europe—Horizon 2020, seven priority challenges in research and innovation that can have a tangible effect on everyday life [6]. Asian countries, also due to their high growth rate of population, will be decisive for the development of sustainable biotechnologies, bio-industries and bio-refineries [7–9]. With the world population approaching about 9.6 billion by 2050 and limited natural reserves, the use of renewable resources is therefore essential for the sustainable supply of



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Selective arene production from transfer hydrogenolysis of benzyl phenyl ether promoted by a co-precipitated Pd/Fe₃O₄ catalyst†

E. Paone,^a C. Espro,^b R. Pietropaolo^a and F. Mauriello^{*a}

The catalytic transfer hydrogenolysis of benzyl phenyl ether has been investigated using Pd/Fe₃O₄ as a heterogeneous catalyst and 2-propanol as a H-donor. After 90 minutes at 240 °C, the cleavage of the ether C–O bond occurs as the only reaction route without hydrogenation of the aromatic ring.

Lignocellulosic biomass containing cellulose, hemicellulose and lignin represents the key renewable substrate for the production of chemicals and biofuels.^{1–4} Lignin is unique among other biomass components, being characterized by an aromatic sub-structure with a large amount of C–O bonds (Fig. 1). As a consequence, one of the major challenges in the catalytic valorization of lignin is the selective cleavage of the C–O bond preserving its aromatic nature.^{5–7}

Among others, catalytic hydrogenolysis processes have gained much attention, representing an important and rather broad area of research in modern green chemistry.⁸ Homogeneous and heterogeneous Ni-based catalysts have found, so far, a potential application in the hydrogenolysis of aromatic ethers by preserving the aromatic ring functionality.^{9–13} Palladium was less investigated, although it provides good results in the liquefaction and hydrodeoxygenation of lignocellulosic biomass.^{14,15} Catalytic systems based on carbon supported bi-metallic Pd–Fe sites were found to be active in the vapor-phase hydrodeoxygenation of guaiacol¹⁶ and cresol,¹⁷ as well as in the cleavage of the C–O bond in benzyl phenyl ether (BPE) and 2-phenethyl phenyl ether (PPE).^{18,19} In the last few years, the Pd/Fe₃O₄ catalyst (prepared by the co-precipitation technique) has shown excellent performance in several catalytic reactions including the catalytic transfer hydrogenolysis (CTH) of polyols and aromatic/aliphatic esters.^{20–28}

The CTH reaction represents an interesting alternative to the direct use of molecular hydrogen with simple alcohols (2-propanol, methanol and ethanol) being an important alternative to traditional H-donor molecules (hydrazine, tetralin, formic acid, cyclohexene, *etc.*).^{29–31} Only a few examples of CTH of aromatic ethers are present in the literature to date.^{21–39} Rinaldi and co-workers have investigated RANEY®-Ni as an efficient catalyst in the transfer hydrodeoxygenation of phenols and aromatic ethers under low-severity conditions.^{32,33} Ford *et al.* studied the conversion of organosolv lignin over the Cu-PMO catalyst by using methanol as the H-donor.^{34,35} A lot of efforts have been done by the Samec research group in the transfer hydrogenolysis of β-O-4 lignin model systems using Pd/C as the catalyst.^{36–38} However, hydrogenated products were always observed, rendering CTH conditions less efficient in producing arene derivatives from aromatic ethers (Scheme S1†).

In this context, the selective cleavage of the C–O bond of benzyl phenyl ether (BPE), a model molecule of the α-O-4 linkage in lignin (Fig. 1), was investigated under CTH conditions using 2-propanol as the H-donor. In the presence of the heterogeneous Pd/Fe₃O₄ catalyst, at 240 °C and within 90 minutes, BPE was fully converted (100% conversion) to toluene

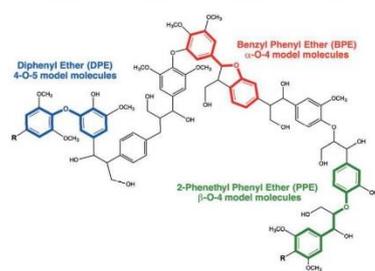


Fig. 1 Benzyl phenyl ether, 2-phenethyl phenyl ether and diphenyl ether as model compounds of C–O lignin linkages.

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Attendance at conferences

Reverse chronological order



XI Congresso AICIng 2018,

Bologna, 9-12 September 2018

Transfer idrogenolisi catalitica di eteri aromatici promossa dal catalizzatore eterogeneo Pd/Ni.

Oral Communication

E. Paone, R. Pietropaolo, A.M. Balu, R. Luque, F. Mauriello.



XI Congresso AICIng 2018,

Bologna, 9-12 September 2018

Catalizzatori bimetallici Pd/Fe per la conversione dell'acido levulinico a γ -valerolattone.

Poster

E. Paone, F. Mauriello, R. Pietropaolo, M.G. Musolino.



XX Congresso Nazionale di Catalisi e della Divisione di Chimica Industriale della SCI,

Milano, 2-5 September 2018

Transfer Hydrogenolysis of lignin derived aromatic ethers promoted by heterogeneous Pd/Ni catalyst.

Oral Communication

E. Paone, R. Pietropaolo, A.M. Balu, R. Luque, F. Mauriello.



Twelfth International Symposium on Heterogeneous Catalysis,

Sofia (Bulgaria), 26-29 August 2018

Transfer hydrogenolysis of aromatic ethers promoted by the bimetallic Pd/Co catalyst.

Oral Communication

F. Mauriello, H. Ariga-Miwa, E. Paone, R. Pietropaolo, S. Takakusagi, K. Asakura.



XXVI Congresso Nazionale della Società Chimica Italiana,

Paestum, 10-14 September 2017

Selective arene production from aromatic ethers promoted by Pd/Fe₃O₄ catalyst under transfer hydrogenolysis conditions.

Oral Communication

E. Paone, R. Pietropaolo, F. Mauriello.

**EUROPACAT 2017 13th European Congress on Catalysis –
- A Bridge to the future,**

Firenze, 27-31 August 2017

*Catalytic transfer hydrogenolysis of diphenyl ether promoted
by the bimetallic Pd/Ni system.*

Poster

E. Paone, R. Pietropaolo, F. Mauriello.



VII Workshop Nazionale AICIng,

Milano, 12-13 June 2017

*Selective transfer hydrogenolysis of benzyl phenyl ether
promoted by Pd/Fe₃O₄ catalyst.*

Oral Communication

E. Paone, R. Pietropaolo, F. Mauriello.



Workshop SciCaSi 2017,

Messina, 9-10 February 2017

*Selective transfer hydrogenolysis of aromatic ethers promoted
by Pd/Fe₃O₄ catalyst.*

Oral Communication

E. Paone, R. Pietropaolo, F. Mauriello.



6° EuCheMS Chemistry Congress,

Siviglia (Spagna), 11-15 September 2016

*Selective transfer hydrogenolysis of benzyl phenyl ether
promoted by heterogeneous Pd/Fe catalyst.*

Poster

E. Paone, R. Pietropaolo, F. Mauriello.



Attendance at Doctoral School

Reverse chronological order



Innovative Catalysis and Sustainability: scientific and socio-economic aspects” Winter School,
Bardonecchia (Italy), 7-11 January 2019



3°SINCHEM Doctorate Winter School,
Bologna (Italy), 15-17 February 2016

Awards



VII Workshop Nazionale AICIng,
Milano, 12-13 June 2017

Award for the best oral presentation

*Selective transfer hydrogenolysis of benzyl phenyl ether
promoted by Pd/Fe₃O₄ catalyst.*

E. Paone, R. Pietropaolo, F. Mauriello.