UNIVERSITY OF BUCHAREST
FACULTY OF CHEMISTRY
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PhD THESIS
ABSTRACT

Lignin fragmentation on multicomponent recyclable catalysts

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Table of content (corresponding to the PhD thesis)

Introduction

The aim of this thesis is to identify catalytic structures able to afford to an advanced fragmentation of lignin to monomers. In order to accomplish this objective the thesis investigated: i) the synthesis of bifunctional magnetic catalysts, easy to be separate and recover from the reaction mixture and to ensure the acidic and metallic character required for the cleavage of the C-O and C-C bonds; ii) the optimization of the catalysts synthesis based on an exhaustive characterization of the catalysts by complementary techniques, such as: BET, XRD, H_2-TPR, XPS, TEM, HADAF, Raman, H_2-TPD, NH_3-DRIFT analysis and catalytic results; iii) the evaluation of the obtained catalysts in lignin fragmentation reactions; iv) the identification and quantification of lignin fragmentation products; v) the investigation of different types of lignin in the presence of the new catalysts; vi) a general pattern of the fragmentation of lignin, from the reactions of the lignin model compounds.

The accomplishments of this thesis are presented in 5 chapters, where the first presents a critical analysis of the reports in the literature and the other 4 chapters discuss the experimental results.

Chapter 1

The biomass derived energy is one of the first forms of used energies. Since ancient times, the biomass has been used to meet various needs, ranging from food and heating of living species till more recently, the production of electricity or its valorification through chemical transformation in industrial processes [1]. This stage has been relatively fast changed into a transition stage where the economy moved to non-renewable materials, which created a strong dependence on fossil resources [2]. This stage contributed to major natural resources depletion, having as side effects global warming and the environmental pollution [1]. Across these negative aspects, oil is still an important source of energy because of its exploitation, transportation and utilization. The oil is the result of biomass long term biodegradation (up to 200 million years). As this process of formation is extremely slow and reserves are finite, the back-transition to renewable raw materials becomes mandatory [3].

The biomass term first appeared in the literature in 1934, in the Journal of Marine Biology Association, introduced by a Russian researcher Bogorov.

Generally, the biomass is defined as a material directly or indirectly derived from plants and considered to be used as an energy source or feedstock [4]. The main fractions selected from the biomass can be grouped into three main categories: i) lignocellulosic materials or woody biomass (extracts from ineligible biomass: bagasse, corn, grass, wood), ii) amorphous sugars (starch, glucose) and iii) triglycerides (vegetal oils) [4]. Lignocellulose is the key structural element of the plants and consists of three main components: cellulose (38-50%), lignin (15-30%) and hemicellulose (23-32%) [5].

Lignin is a three-dimensional polymeric compound of the cell spaces providing resistance to plant tissue [6]. Structural, this polymer consists of three main monolignols: p-coumaryl alcohol, coniferyl alcohol and synaphyl alcohol. This structure has also been confirmed by retrosynthesis from enzymatic polymerization [7]. Extraction of lignin from biomass is known as delignification and involves the desintegration of lignocellulosic material into fibrous components [8]. Depending on the nature of the solvent, chemicals delignification processes are gruped into two main categories, namely those using organic solvents [9] and those using aqueous solvents [10]. In the turn, chemical processes of aqueous delignification include alkaline delignification (Kraft pulping) and delignification in the presence of sulfite. By chemical delignification is achieved a selective separation of lignin without the degradation of carbohydrates [11].

Further fragmentation of lignin can lead to aromatic chemicals and even hydrocarbons. However, the polyphenolic structure, very stable from the chemical point of view, requires energetic reaction conditions. At the same time, the high oxygen content prevents the direct use of the depolymerization products as traditional fuel substitutes or additives [12].

Until now, fragmentation of lignin has been achieved taking into consideration mainly three strategies:

1. Combustion of lignin to the synthesis gas, followed by the Fisher-Tropsh synthesis [13,14];
2. Rapid pyrolysis (flash pyrolysis) with bioil production [15,16];
3. Hydrogenolysis with fragmentation of lignin into a cocktail of monomeric and / or oligomeric units [17-20].

The first two strategies are characterized by more severe working conditions, which have several disadvantages: i) an energy consumption which can reach up to 60% of the biomass energy content; ii) generation of the secondary reactions. These reactions are the consequence of the recombination of the radicals with the formation of new carbon-carbon bonds, resulting in the production of coke [21].

Others methods considered for the fragmentation of lignin are hydrolysis and oxidation. Biochemical modification considered oxidation and microbial conversion are also used. Except for gasification and pyrolysis, all other directions require the presence of a catalyst. Therefore, maximizing the catalyst activity under as gentle conditions as possible is extremely important. The use of unconventional techniques, such as microwaves, ultrasounds, or working with modified solvents such as organosolvents, may have important contributions in these processes [18].

Repolymerization reactions are an impediment for the chemical processes associeted to lignin fragmentation. To eliminate these, they have proposed solutions to protect the reactive functional groups. For lignin, depending on the applied treatment, these may be hydroxyl, phenolic or acidic groups. Compounds used in this purpose were either organic or inorganic (eg boronic acid to protect OH groups or alcohols / phenols to protect the acids ones) [22].

Early studies on heterogeneous catalytic lignin hydrogenolysis were reported in 1938 by Harris and Adkins an a copper chromium catalyst, using lignin from poplar wood as a substrate [23]. Further, the role of the catalyst was diversified and its application extended.

The fragmentation of lignin or bioil via catalytic hydrogenolysis / hydrodeoxygenation leads to phenolic compounds or cyclic ketones further used for the production of resins, solvents, levoglucosan and levoglucosone [23] or aromatic hydrocarbons [24]. The resulting fragments can also be used for the production of fuels [25]. The reactivity of the oxygen-containing chemical compounds to hydrogenation / hydrogenolysis is different depending on the nature of the functional groups. Furthermore, these reactions can be accompanied by competing reactions leading to a thermal decomposition untill CO, CO_2 or H_2O [26].

The catalysts used in hydrodeoxygenation reactions have to accomplish a number of properties [27]:

- high activity for hydrodeoxygenation reactions - with a direct effect on the decrease of the reactor size and increase of the efficiency;

- resistance to coking and ability to reduce its formation - with a direct effect on the reduction of the time of the regenerative operations;
- high stability in water;
- thermal stability allowing the regeneration via simple processes such as heating in air or steam treatment;
- resistance to poisoning with a direct effect on the catalyst life [27];

Catalytic hydrolysis is a process dependent on the reaction conditions and on the initial lignin structure. It can occur in an acidic or basic medium using lignin as starting material or model compounds, and it is believed to be based on the etheric bond breakage [21, 28-31]. Other strategies addressed in lignin fragmentation are the enzymatic hydrolysis [32,33] and anaerobic microbial degradation [34]. Catalytic oxidation [35, 36] represents another direction addressed for the same purpose of an advanced fragmentation.

The role of the solvent in these processes is very important, irrespective to approached strategy. The solvent directly influences the mechanism of the lignin fragmentation [21]. This has been confirmed by the investigation of a large variety of solvents, including water [36], organic [37] or supercritical solvents (methanol / ethanol) [38, 39].

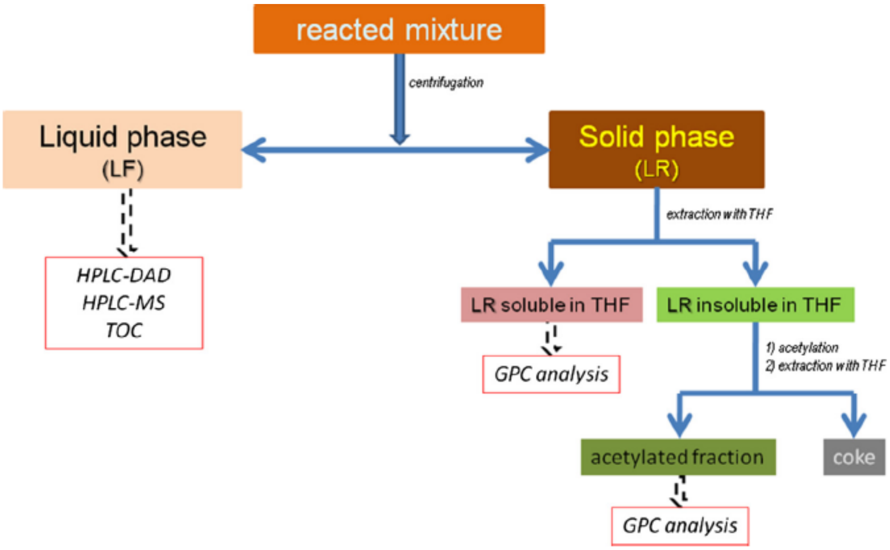
Chapter 2

The general aim of the studies presented in this chapter was to investigate the superparamagnetic catalysts for the fragmentation of lignin in the liquid phase. In order to achieve this goal, magnetic nanoparticles were encapsulated in a layer of niobium oxide, with double role: i) to protect magnetic nanoparticles and ii) to generate an acidic function. Cobalt nanoparticles were deposited onto the resulting composite in order to induce the catalytic function required for the C-C bond hydrogenolysis. Cobalt has been reported in the literature for its activity in the hydrogenolysis of both C-C and C-O bonds [40-43] while niobium oxide for its catalytic properties in reactions taking place in aqueous medium (acidity, activity, stability and insolubility) [44]. Nb_2O_5 contains both Lewis and Bronsted acid centers. As a support, it can also lead to strong metal / support interactions (SMI), which can provide catalytic hydrogenation active sites [45].

For the elucidation of their catalytic properties, the $Co@Nb_2O_5@Fe_3O_4$ composites have been characterized by different techniques such as: measurements of the surface area, XRD, Raman spectroscopy and NH_3-DRIFT spectroscopy, XPS and Mössbauer and electron microscopy (TEM, HRTEM, HADAF, EDX).

The lignin used in the fragmentation process was extracted by an acid process [46] from Mischanthus X Giganteus (cultivated in Romania in the Sfântu Gheorghe area and harvested in September 2014). The lignin fragmentation was performed in a 16 mL autoclave (from Hell) with continuous stirring using between 10 till 20 mg catalyst and various lignin / catalyst molar ratios (ranging from 8.4 to 67.2) dispersed in 5 mL of water or organic solvent (methanol, ethanol or 1,4-dioxane). The reactions were carried out at temperatures ranging from room temperature to 230 ° C and pressures from 2 to 20 bar H_2 for a reaction time of 1.5 till 24 h. The reagents were introduced into the autoclave under an inert atmosphere, in the presence of nitrogen, then the autoclave was flushed by hydrogen several times before bringing the pressure at which the reaction was carried out.

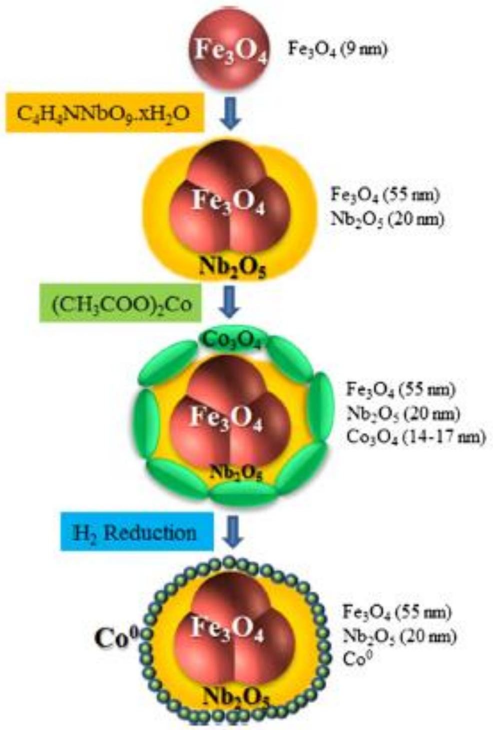
Analytical measurements for the identification and quantification of the fragments resulted from the depolymerization of lignin have been performed both in liquid and solid phase. Analysis of remaining solid phase residues (residual lignin - LR) was performed after the extraction with THF under the following conditions: the solid phase was separated from the reaction mixture by centrifugation, then the solid was dried at 70 ° C under vacuum, until a constant mass has been achieved. Then, 1 mL of THF was added over the dry solid and the mixture was stirred for 1 h. The obtained two phases were separated by centrifugation and the resulting solid phase (THF insoluble LR) was acetylated, while the liquid phase (THF-soluble LR) was filtered and analyzed on GPC (Scheme 1).



Scheme 1. Pretreatment and analysis of the reaction mixture

Analysis of these phases was performed by GPC using an Agilent Technologies (Model 1260) equipped with two columns (Zorbax PSM 60-S, 6.5 x 250 mm, 5 µm and Polargel-M, 300 x 7.5 mm) and a detection unit Multiple (260 GPC / SEC MDS contains the RID, LS, and VS detectors). GPC working conditions were set at optimum values, resulting in the use of tetrahydrofuran as the mobile phase at a flow rate of 1 mL / min. The GPC system was calibrated using polystyrene standards, with masses ranging in the range of 162-1,000,000 g/mol, providing a good accuracy of measurements for compounds with MW > 1000. The mean molecular weights for the obtained lignin fragments were calculated based on the GPC chromatograms.

Corroborating the results obtained from the catalyst characterization provides a complete picture of the x%Co@Nb_2O_5@Fe_3O_4 catalyst structure has been provided (Scheme 2).



Scheme 2. Steps of the synthesis of Co@Nb_2O_5@Fe_3O_4 catalysts

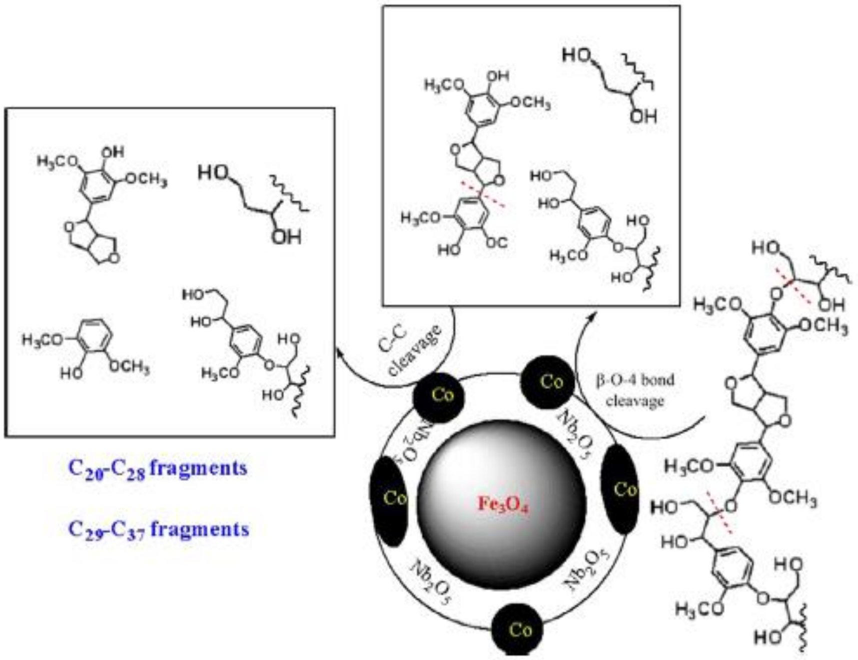
The magnetic core of the catalysts consists of magnetic nanoparticles with an average size of 10 nm. Mössbauer measurements have shown that these particles are composed of a mixture of magnetite and maghemite. Subsequent deposition of niobium produces a Nb_2O_5@ Fe_3O_4 magnetic particle generated by the particle fusion. The formation of composites has been demonstrated both by X-ray diffraction and surface measurements, as well as by the TEM images. The niobium oxide in these materials exists as a continuous amorphous layer covering the magnetic core. This was demonstrated by Raman, XRD and the TEM analysis. Finally, deposition of cobalt leads firstly to the formation of Co_3O_4 nanoparticles. Reducing these particles with hydrogen leads to very small cobalt nanoparticles (confirmed by XRD and HADAF measurements). The characterization of the catalysts confirmed the bifunctional properties generated by the association of Lewis and Brønsted acid centers on the surface of niobium with finely dispersed cobalt nanoparticles.

Magnetic nanoparticles exhibited catalytic activity in fragmentation leading to a conversion of 15%. This behavior can be associated with the presence of maghemite, which is a defective structure derived from magnetite. The fragmentation in the presence of these particles only led to large C38-C40 fragments. Compared to Fe_3O_4, niobium is less active (5% conversion), some of the lignin remaining completely untransformated. The presence of acidity allows fragmentation of lignin in the presence of this oxide to small fragments (yields in C20-C28 fragments reaching up to 40%). The catalytic behavior of Nb_2O_5@Fe_3O_4 composite is very close to that of Nb_2O_5 (7% conversion and a similar distribution of the reaction products). The use of Nb_2O_5@Fe_3O_4 as a catalyst leads to a solid phase containing very large molecular weight fragments. The activity of the Co@Nb_2O_5@Fe_3O_4 catalysts in this reaction is attributed to the participation of the acidic centers of niobium and cobalt metal centers, combining the ability of niobium to catalyze the acid hydrolysis of β-O-4' bonds with affinity of cobalt to facilitate the breakage of C-C bond by hydrogenolysis. The catalysts with this composition allowed more than half of lignin (Cp = 53%) to be transformed into small fragments (over 90% fragments C20-C28 and C29-C37). The performance of these catalysts depends on the concentration of the deposited metal and the reaction conditions (temperature, H_2 pressure).

The optimization of the catalyst composition led to the conclusion that 4% wt Co represents the optimal concentration. The use of this catalyst allows a selectivity of over 96% in fragments C20-C28 and C29-C37. This optimal behavior corresponds to a particle size for Co_3O_4 of about 17 nm and a Co^0 / Co^{2+} ratio, measured by XPS, of 0.21. Higher concentrations of cobalt lead to particles with large Co^0 / Co^{2+} sizes and ratios.

Based on these results, it is possible to consider the mechanism of the fragmentation of lignin in the presence of the catalysts investigated in this study by the sequences included in Scheme 4.

The presented reaction mechanism suggests the presence of two parallel reactions: hydrolysis of β-O-4' linkages, which is catalysed by niobia from the thin layer and hydrogenolysis of the C-C bonds that occurrs in the presence of cobalt. This tandem lead to the formation of the C20-C28 fragments and is followed by the dimerization of these entities. The fragmentation mechanism proposed in Scheme 3 was also confirmed by the collected ^{1}H-^{13}C-HMQC spectra.



Scheme 3. The lignin fragmentation mechanism in the presence of the $Co@Nb_2O_5@Fe_3O_4$ catalysts

In conclusion, the addition of cobalt generates $Co@Nb_2O_5@Fe_3O_4$ catalysts able to effectively depolymerize the lignin. This behavior is based on the ability of niobia to catalyze the acid hydrolysis of β-O-4' bonds and of cobalt to break the C-C bonds by hydrogenolysis. Optimising the catalytic tests leads to the conclusion that for cobalt the optimal concentration was 4 wt%. In the presence of this catalyst at 180° C and 10 atm hydrogen a conversion of 53% and a selectivity of 96% in C20-C28 and C29-C37 fragments has been obtained. The investigated catalysts were fully recyclable, as demonstrated by six successive cycles of reaction. ICP-OES analyzes did not confirm the leaching of the elements contained in the catalyst composition.

Chapter 3

Hydrodeoxygenation is a way remove oxygen in the presence of a high hydrogen pressure (4-10 bar) and a relatively high temperature (300-500° C) [47]. Over the years, this reaction was investigated in presence of a variety of transition metals. The main drawbacks of their use are the deactivation of the catalyst due to the coke formation, hydrothermal instability and catalyst sintering [48]. Therefore, identifying more stable, recyclable catalysts with activity and selectivity in order to obtain the desired products is required. This aim can only be achieved by combining the active centers of the support with those of the promoter [49].

Among the metals used for this reaction, rhenium is known for its ability to catalyze the cleavage of the heteroatomic X-C linkages [50-52], but also as a selective hydrogenation catalyst [53-57]. Rhenium also favors reactions that can cleave C-C and C-H aromatic linkages [58]. Another remarkable property of rhenium oxide is its ability to selectively reduce carboxyl groups without affecting the aromatic rings [59].

The use of rhenium as an active catalyst (active species dispersed on the support) [60] is based on two effects: (i) the capture of strong chemisorbed species, (ii) the ability to interact with a second metal present in the catalyst structure that is facilited by its dispersion in small and more active catalytic species [61]. Rhenium exhibits activity for the hydrogenolysis of the C-O bond [62], but has the disadvantage of a high volatility [63].

The literature assume the activity and selectivity of bimetallic catalysts containing rhenium to the decrease of the hydrogen enthalpy value on its surface, which favors the desorption of the products leaving more accessible centers for the catalytic reactions [64].

As mentioned above, rhenium is usually used together with a second transition or noble metal (Rh, Ru, Pt or Pd) deposited on a suitable support (C, SiO_2 and Al_2O_3). In these combinations, rhenium is a promoter for noble metal. For the glycerol conversion using Pt-Re/C catalysts the presence of Re facilitates the hydrogenolysis of the C-O bonds due to itability to bind preferentially to hydroxyl groups [65,66]. Then, these species interact in a secondary step with the hydrogen dissociated and activated by the second noble metal [67,68], resulting in an improvement in both the selectivity and activity [59]. The effect of the Lewis acidity generated by rhenium on the hydrogenolysis of the oxygenated compounds was also demonstrated by the increase of the selectivity for the of rhenium-ruthenium bimetallic catalysts [49]. The role of support is also important for achieving a high activity of rhenium by controlling the particle size [53]. The support also contributes to improving the stability and lifetime of the catalyst as well as the selectivity. This is also the reason why many reforming catalysts use rhenium as a promoter for platinum-based alumina catalysts [69].

The aim of the studies presented in this chapter was to determine the role of rhenium as a promoter for the Co@Nb_2O_5@Fe_3O_4 catalysts in the fragmentation of lignin reaction. The investigation of the reaction mechanism in the presence of these catalysts for the fragmentation of lignin was a second objective.

The prepared catalysts contain pores large enough to allow the access of the lignin fragments to the active sites. Under these conditions, the deposition of rhenium and cobalt in a total metallic concentration greater than 7% does not produce significant differences in the textural properties of the catalysts, irrespective of the method of depositing rhenium. Both cobalt and rhenium have a high degree of dispersion. The deposition of rhenium starting by rhenium chloride and impregnation or precipitation does not influence the structure of the Co@Nb_2O_5@ Fe_3O_4 catalysts or the magnetic core that remains unaffected. The characterizations performed have shown that the very thin layer of niobium oxide is able to protect the magnetite. Instead, starting from ammonium perrenate, as a precursor, there were identified changes in the support and the formation of Fe_3O_4 in a new phase containing metallic species. This was confirmed by XPS analysis. Increasing the concentration of rhenium leads to the modification of the Re / Fe atomic ratio confirming the catalytic role of the rhenium in this process. The same XPS analysis showed that after the reduction with hydrogen, rhenium is present in various oxidation states. The samples prepared by ImC and ImA methods showed a higher degree of reduction, and the decrease in the cobalt content had the effect of increasing the content in reduced rhenium. For the catalysts prepared by PP, the presence of metallic rhenium was not observed, although they were reduced under the same conditions. As in the case of rhenium, XPS analysis of cobalt showed the presence of a mixture of oxidized and reduced species. Samples prepared by ImC and ImA appear to exhibit a higher degree of reduction, but the decrease in concentration of cobalt corresponds to a lower amount of reduced cobalt.

These results were also confirmed by H_2-TPR, NH_3-TPD and TEM analyzes. The H_2-TPR profiles confirmed the increase in the amount of chemisorbed hydrogen for the ImC and ImA samples, while the adsorption of ammonia showed an increase in the acidity for the catalysts prepared by the PP method. Also, the profiles of these samples corresponded to desorptions at high temperatures, thus confirming the presence of stronger acid sites.

The catalytic tests have shown a good correlation with the structural characteristics, confirming the role of the composition and the method of depositing rhenium. Thus, catalysts synthesized by impregnation (ImC) or precipitation-deposition (PP), starting from rhenium chloride, exhibited a catalytic activity superior to those prepared by impregnation starting from ammonium perhenate (ImA). From a structural point of view, this corresponds to catalysts in which rhenium coexists in different oxidation states (including Re (0)), along with cobalt. Rhenium's role in the fragmentation of lignin is obvious. In the previous chapter it was shown that in the presence of $Co@Nb_2O_5@Fe_3O_4$ monometallic catalysts a maximum yield of 40% for water soluble fractions was obtained at a cobalt concentration of 4% wt. Adding rhenium led to increased yields in small fragments (LF), that has been accompanied by a complete recovery of the catalyst. The comparison of the bimetallic $3\%Re@2\%Co@Nb_2O_5@Fe_3O_4$ with monometallic catalysts with 3% wt Re and 2% wt Co, under similar reaction conditions indicated a synergistic effect due to the presence of the two metals. The bimetallic catalyst leads to a 85% LF yield, which is greater than the sum of the yields obtained in the presence of the individual monometallic catalysts (Figure 1).

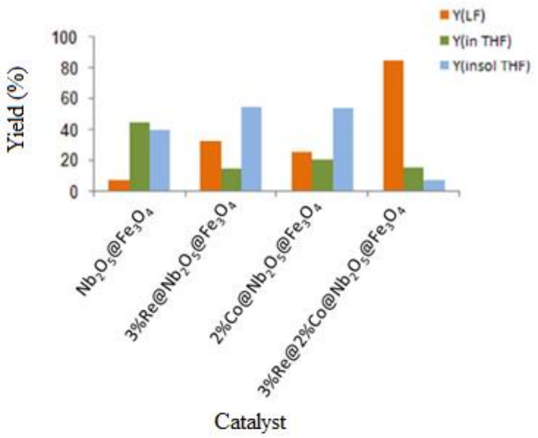
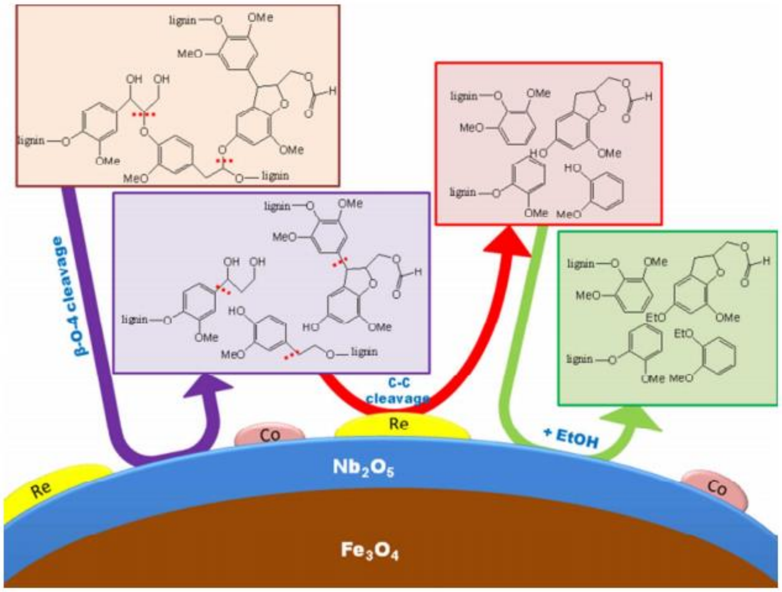


Figure 1. Evaluation of the catalytic behavior of the composition based on the distribution of lignin-derived fragments: water-soluble (Y (LF), orange, soluble in THF (Y (in THF, green)), insoluble in THF (X) is the catalyst composition (0.02 g of catalyst, 0.01 g of lignin, 2.5 mL of H_2O, 180°C, 10 bar).

Recent studies on the role of rhenium upon the activation of platinum for glycerol reforming and hydrogenolysis have shown that rhenium activates the C-O bond when it is in a dispersed state near by platinum [70]. These species are supposed to act as Bronsted acid centers [71]. In this study, none of the investigated catalysts showed Bronsted acid centers. Unconcerned of the deposited metal concentration, the synthesized catalysts showed only Lewis centers of different strengths (weak, medium and strong). The distribution of these centers is influenced by the metal concentration and the rhenium deposition method. XPS analysis showed that among the investigated catalysts, the ImC series is the most active and contains metallic rhenium. Thus, the synergism between the oxidized and reduced metal species of rhenium and cobalt allows the catalysts to exhibit a high activity in the production of low molecular weight soluble fragments. This positive effect, however, is limited to a maximum concentration of 3%wt of each element. Higher concentrations have shown a negative effect on the fragmentation of lignin.

Corroborating these results, the mechanism outlined in Scheme 4 has been proposed. The variation of reaction conditions (solvent, reaction temperature, pressure, volume of reaction) allow to the optimization of the reaction parameters in order to obtain an advanced lignin fragmentation.



Scheme 4. Lignin fragmentation mechanism in the presence of $Re@Co@Nb_2O_5@Fe_3O_4$ multifunctional catalysts: The sequence catalyses the breakage of the C-C bond, while Nb_2O_5 contributes to the breakage of β-O-4 bond, and the resulting fragments are stabilized in the presence of ethanol.

The deposition of rhenium and cobalt on $Nb_2O_5@Fe_3O_4$ led to multifunctional catalysts in which the presence of magnetite ensures the recovery of the catalysts at the end of the reaction, niobium and rhenium provide the acidity necessary for the cleavage of the etheric groups and cobalt and rhenium contribute to the hydrogenolysis of C-O bonds and hydrocracking of the C-C bonds. The catalysts thus obtained showed a particle size in the order of nanometer and pores enough large to allow the access of the lignin fragments to the active surface. The cooperation between rhenium and cobalt was highlighted in the reduction of the two metals. The presence of cobalt favors the distribution of the rhenium in the optimal oxidation state required by this process. Rhenium distribution is correlated with the deposition procedure.

Testing of the ImC, ImA and PP series catalysts in the fragmentation of lignin confirmed the role of the structural properties. The catalysts of the ImC series exhibited superior catalytic activity compared to those prepared by the ImA or PP methods. In this series, the 3% Re@2%Co ImC catalyst led to a more advanced conversion of lignin (85% yield in LF, 15.5% yield in soluble THF in LR and 14.5% yield in THF insoluble LR). With the exception of the 3%Re@2%Co ImC catalyst, for the other catalysts from the ImC and ImA series, in the liquid phase, prevails compounds with molecular weights between 400 and 600 Da. In turn, the catalysts prepared by PP led to a more advanced fragmentation of the lignin giving fragments with molecular weights ranging from 200 to 400 Da. These results confirmed the synergism between the specific acidity induced by rhenium species in catalysts and the participation of reduced metals. In the solid phase, for all tested catalysts, the prevalence of compounds with molecular weights ranging from 400 to 1000 Da was observed.

The solvent has an important role because it is responsible for the transport of the fragments. The use of ethanol as solvent has led to the best reults.

Another important feature of these catalysts is the complete recovery by applying an external magnet, followed by a simple washing with water. It has been observed that they can be re-used in six reaction cycles without affecting the activity or selectivity.

Chapter 4

In Chapter 3 it has been shown that the use of magnetic nanoparticles can provide catalyst recovery, while rhenium, niobium oxide and cobalt confer the catalytic functions. The acidity of rhenium is associated to a Bronsted acidity corresponding to of the hydroxylated rhenium atoms derived from the Re-O bonds. The result is the formation of O-H groups, as well as a high electron-affinity for the conjugate base [72]. The acidity of the rhenium catalysts is also influenced by the metal-support interaction and the dispersion of the active metal species [73]. Also, the interaction between rhenium oxides and a secondary metal influences the surface properties of the catalytic materials [74].

Consequently, the use of rhenium in the bifunctional catalysts leads to an increase in activity over the C-O bond breaking reactions and the hydrogenation of the carboxylic acids, which is consistent with its oxophilic character. The hydrogenation of 2-methoxyphenol is an example illustrating the ability of rhenium in this process[75]. At the same time, metallic rhenium acts as Lewis acids due to the low occupancy of the d band [76].

Based on the results previously reported [77,78] and taking into account the intrinsic catalytic activity of rhenium, the aim of this chapter was to optimize the catalyst by depositing rhenium onto a magnetic center incorporated in a layer of silica ($SiO_2@Fe_3O_4$). The resulting catalysts were investigated in the hydrolysis / hydrogenolysis of lignin. For this purpose, rhenium was deposited on these catalysts using both impregnation and precipitation-deposition as methods. Another objective was the use of water as a solvent and the investigation of these catalysts in the fragmentation of different types of lignin.

The characterization of the catalysts has shown that the coating of magnetite with silica leads to the protection of the magnetic core of the catalysts. The XRD diffractograms of 2% $wtRe@SiO_2@Fe_3O_4$ catalysts before and after the reduction with hydrogen show the characteristic lines of magnetite in aweel preserved state. Lines at 2 theta 35.5, 43 and 53^o correspond to the crystallographic faces (311), (400) and (422) of Fe_3O_4 [79]. No reduction of the iron species has been observed, thus confirming the protection role of the silica layer. The presence of silica in these diffractograms is very discret, with only a small shoulder at 2 theta between 20 and 30 2Ѳ, corresponding to its amorphous nature. The corresponding lines of rhenim are absent in these diffractograms as a result of the very small particle size.

The method of depositing rhenium does not affect the magnetic properties of the synthesized catalysts, but it has an effect on the particle size of the resulting catalytic materials. Regardless of the method, rhenium is dispersed on the surface of the catalyst under the PP method, just below the detection limit (e.g., XRD or XPS). The acidity of these catalysts is due to the presence of rhenium, which generates a weak Bronsted acidity, as evidenced by the NH_3-TPD analysis. The H_2-TPD experiments have demonstrated the ability of these catalysts to chemisorb hydrogen.

The different types of lignins tested in the fragmentation reactions were characterized by FTIR and DTA-TG. Through these characterizations it has been confirmed that the complex structure of lignin depends on the source of lignocellulosic materials and the extraction method.

Lignin fragmentation is also influenced by the synthesis method of the catalysts and the concentration of rhenium in their composition (Figures 2 and 3).

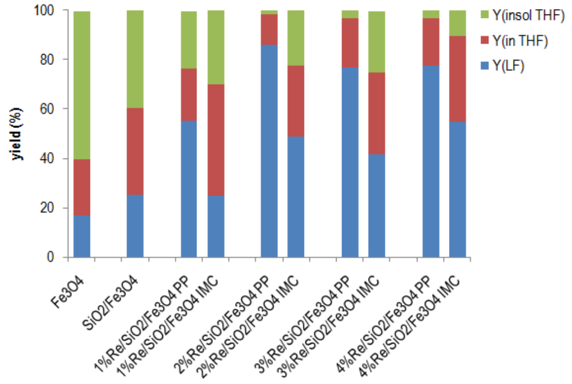


Figure 2. The yields of the lignin fragmentation process in the presence of synthesized catalysts. Experimental conditions: 0.01 g of catalyst, 0.4 g of L1, 5 mL of solvent, 180 ° C, 10 atm and 6 h.

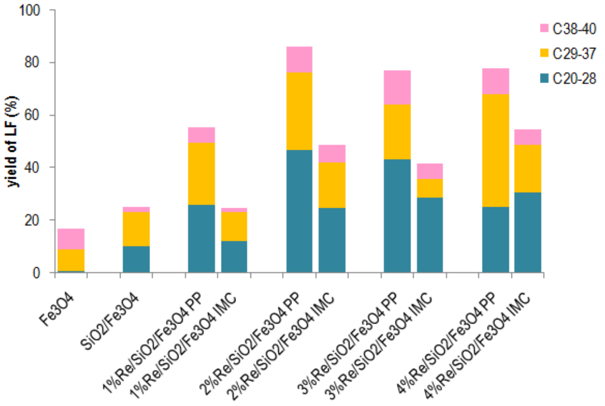


Figure 3. The yields of LF fragments in the presence of synthesized catalysts. Experimental conditions: 0.01 g of catalyst, 0.4 g of L1, 5 mL of solvent, 180 ° C, 10 atm and 6 h.

As a general trend, the catalysts prepared by the PP method afforded an advanced fragmentation of lignin with high yields in soluble / insoluble THF fractions. The highest yield was of 98% for the 2%wtRe@SiO$_2$@Fe$_3$O$_4$-PP catalyst. The optimization of the fragmentation of lignin in the presence of this catalyst was accomplished by the optimisation of the reaction parameters such as temperature, hydrogen pressure or reaction time. The optimal reaction temperature (6h) was established under the conditions of the fragmentation of lignin at temperatures between 100-230ºC. At higher reaction temperatures, the repolymerisation occurs leading to decreased yields in compounds with small molecular weights. The hydrogen pressures higher than 10 atm does not significantly affect the yields. The change in the reaction time indicates that for the short times there is a progressive increase in the yield in small fragments. The maximum yield (50%) was obtained for the 6 hour reaction.

Also, to highlight the versatility of the studied catalysts, different types of lignin were tested, with the highest degree of fragmentation resulting for lignins extracted by the acid or Organosolv process (Figure 4). This behavior has been associated to higher concentrations of ether linkages in these structures, which favor a higher degree of fragmentation.

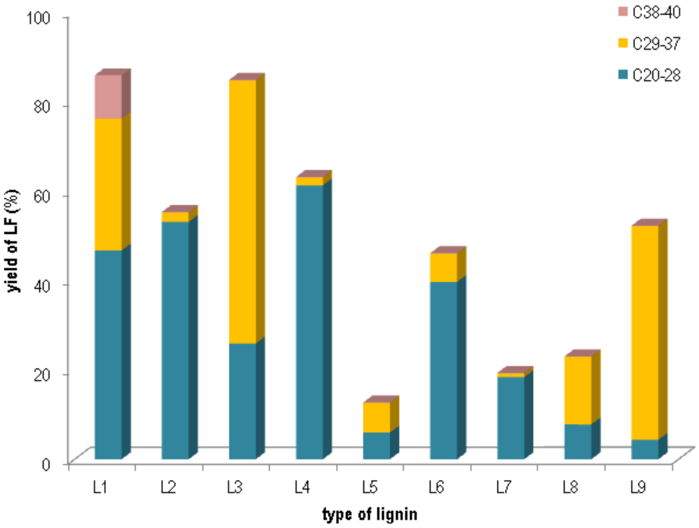


Figure 4. Fragmentation of different types of lignin: distribution of lignin fragments in the aqueous phase. Experimental conditions: 0.01 g 2 wt% Re@SiO_2@Fe_3O_4-PP, 0.4 g lignin, 5 mL solvent, 180 ° C, 10 atm and 6 h.

In conclusion, the simplification of the catalyst was achieved by depositing rhenium on a magnetic core encapsulated in a layer of silica (SiO_2@Fe_3O_4) and its use in the hydrolysis / hydrogenolysis reaction of lignin has shown that rhenium is able to produce the fragmentation of lignin under the investigated working conditions .

Chapter 5

The natural degradation of lignin includes a series of reactions, such as: cleavage of etheric linkage, hydroxylation of aromatic rings, oxidation of alkyl chains to aldehydes or carboxylic acids. Further, aldehydes and organic acids can be enzymatically decarboxylated, forming polyphenol or can be mineralized with the formation of CO_2. Polyphenols are reactive compounds able to form covalent bonds with nucleophilic compounds. The incomplete oxidation of these may generate radicals that lead to polymerization reactions [80]. Most lignin phenolic units contain guaiacol, veratrol or 2,6-dimethoxyphenol. Therefore, the presence of these oxygenated substituents in the ortho position is responsible for the formation of coke during pyrolysis [81].

3,4-Dihydroxybenzaldehyde can also participated to polymerization reactions under electrochemical conditions based on a mechanism whose first stage is the formation of phenoxy radicals. These radicals participate in coupling reactions resulting in dimeric compounds or long polymeric chain products. Oxidation of phenoxy radicals leads to the formation of monocations, which together with phenol afford the formation of long chain polymers [82]. On the other side, 2-methoxyphenol (guaiacol) is attently use as a model compound for the deoxygenation processes of lignin or biogas derived from lignin [83].

The use of guaiacol as a model compound has been investigated by different groups for more than 20 years (Delmon et al.). According to these studies, the first step in the conversion of guaiacol is the breakage of the O-CH_3 bond, which results in the catechol formation [84]. The apparent activation energy for the conversion of guaiacol (14-17 Kcal / mol) is less than that required to break the C-O bond (27 Kcal / mol) [85], which leads to the idea that the polymerization reaction occurs from the beginning of the chemical process of the transformation of guaiacol [86]. According to literature data, condensation reactions take place at low activation energies [87]. Also, the formed catechol has the tendency to generate condensation reactions, with the formation of products with large molecular weights. At the same time, it has been suggested that the conversion of guaiacol is strongly influenced by the interactions between the support and the catalytically active centers. Thus, in the presence of catalysts containing rhenium or rhenium sulfide deposited on silica they were reported to high conversions of phenol and catechol as intermediate product [88]. The activity of rhenium in this reaction is based on the acidity of the oxidized or sulphated species and the presence of coordinate unsaturated centers. The interaction of hydroxyl groups in the guaiacol structure with the Lewis acid centers leads to an transfer of a pair of electrons from the oxygen to the metal center. This results in: (a) increasing the electronic density near the substituents of the aromatic ring and (b) facilitating the cleavage of the etheric C-O linkage [89].

In the presence of fatty acids, the same catalysts can catalyze the chemical modification of lignin by the esterification of the hydroxyl groups. Such as esterification may modify the interfacial adhesion properties with application in the adhesives and polymer industries [90].

Also, the esterification of lignin increases its hydrophobicity and solubility in organic solvents. By esterification the number of hydrogen bonds is also reduced, and the lignin thermoplasticity increases [91].

The aim of the investigations presented in this chapter was to expand the application of the catalysts presented in Chapter 3 for the reactions of 3,4-dihydroxybenzaldehyde and guaiacol, considered as model compounds of lignin. These reactions were carried out under similar conditions to those in which lignin was used as starting material. Since the structural modification of lignin allows the possibility of use as a new polymeric material, another objective of this study was the acylation of lignin with octanoic acid in the presence of the catalysts described above.

The results obtained confirmed the role of rhenium in the fragmentation of lignin. The presence and activity of its active sites was also confirmed in repolimerization reactions using 3,4-dihydroxybenzaldehyde and guaiacol as molecules. Rhenium favors repolimerization reactions, while cobalt inhibits them to some extent. In the absence of the catalysts, 3,4-dihydroxybenzaldehyde dimerizes leading to a mixture of C20-C28 compounds (Figure 5). In the presence of rhenium the catalytic polymerization is more advanced (3% Re@SiO_2@Fe_3O_4, 3% Re@Nb_2O_5@Fe_3O_4, 3% Re @Nb_2O_5@SiO_2@Fe_3O_4) leading to C38-C40 compounds with an almost total selectivity (> 98%). An additional argument supporting the contribution of rhenium in the polymerization process is the decrease in the selectivity to C38-40 compounds with the increase of the concentration of cobalt (from 99% in the absence of Co to 0% for the catalyst containing 4% Co). Finally, catalytic activity is dependent on the degree of the reduction of the metal precursor, the shape and size of the metal particles [92].

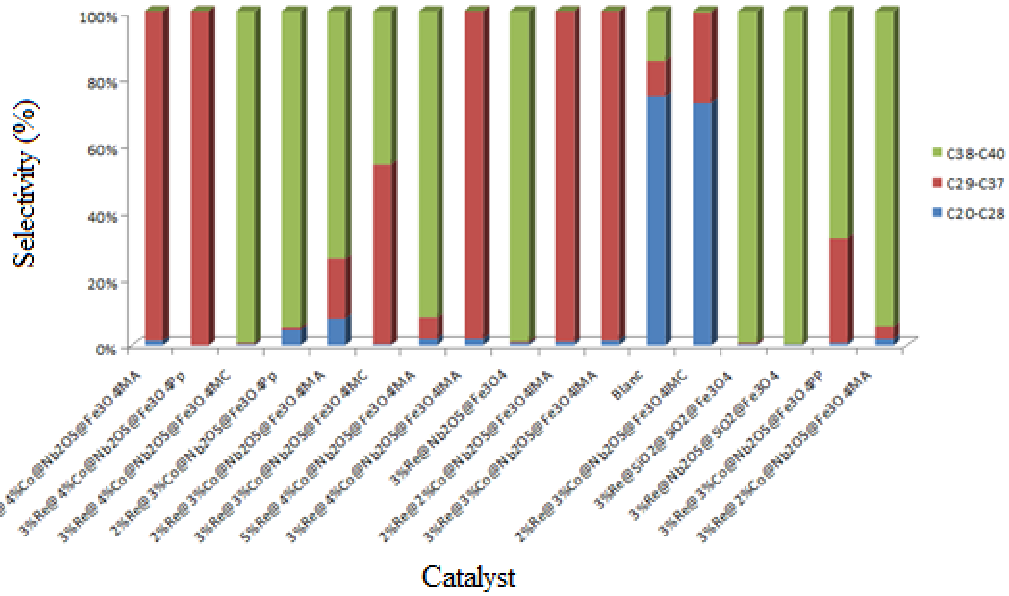
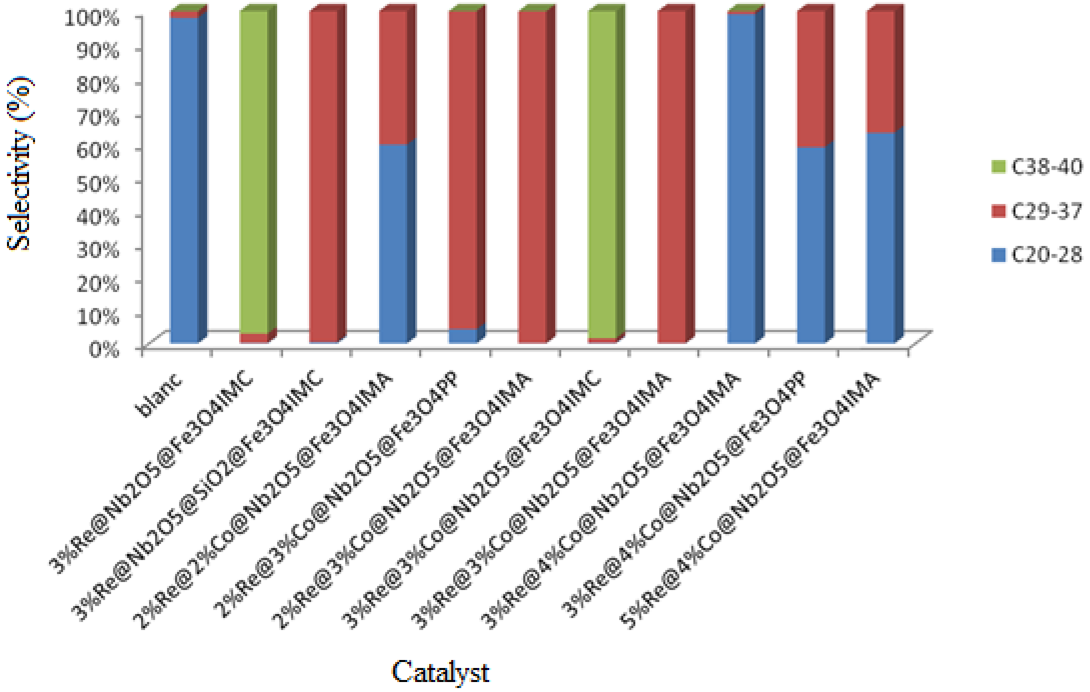


Figure 5. Distribution of molecular fragments from the liquid phase identified by conversion of 3,4-dihydroxybenzaldehyde (0.02g of catalyst, 0.01g of 3,4-dihydroxybenzaldehyde, 2.5ml of water, 10 bar, 180ºC, 6h)

Concerning guaiacol (Figure 6), the non-catalytic reaction leads to the formation of the dimer, whereas rhenium supported on niobia or silica catalysts leads to C38-C40 compounds with a selectivity of 97%. Also, in this case, a low concentration of cobalt in the catalyst composition is associated with a more advanced polymerization of guaiacol. This provides an additional confirmation of the previous observation that in the presence of cobalt the polymerization reaction is blocked.



Another aspect followed in this chapter was the fragmentation of lignin coupled with the acylation reaction of the resulted fragments in the presence of the same catalysts. Adding octanoic acid to the reaction mixture resulted in a different distribution of the reaction products in the liquid phase, showing that these catalysts are able to produce the fragmentation of lignin even in the presence of an acylating agent (Figure 7). Also, the concentration of the metal species in the composition of the catalysts, as well as their synthesis method, influence the degree of the fragmentation of the lignin. The use of catalysts containing niobium oxide coated magnetic particles prior to the deposition of rhenium leads to higher selectivity for the C38-C40 compounds as compared to the use of catalysts containing silica-coated particles (62% vs 11%).

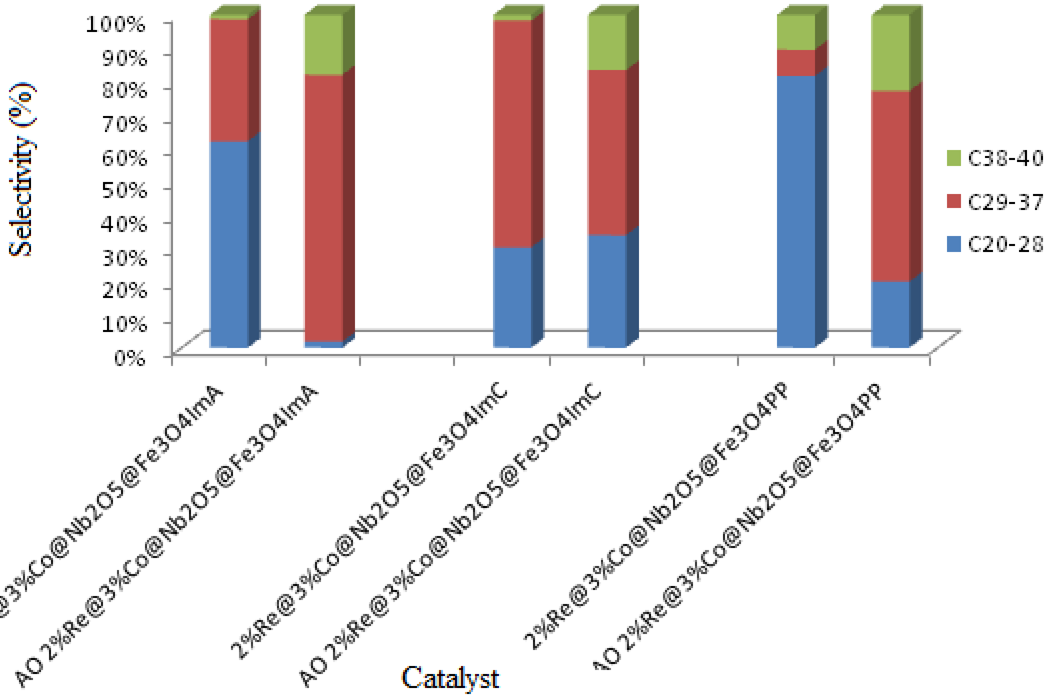


Figure 7. Distribution of liquid fragments from the liquid phase identified after lignin conversion in the presence of 2% Re@3% Co@Nb_2O_5@Fe_3O_4 catalysts, synthesized by ImA, ImC and PP respectively (0.02g of catalyst, 0.01g of lignin, 2.5 mL water, 10 bar, 180° C, 6h) in the presence of (AO) / absence of octanoic acid (11 µL)

This behavior can be explained based on the higher acidity of the niobia favoring the acylation reaction of the fragments obtained by lignin depolymerization.

Conclusions

The aim of this thesis was to identify heterogeneous catalytic structures able to produce an advanced fragmentation of the lignin to monomers. Another major objective of this thesis was to synthesize separable catalysts from the solid and recyclable mixtures. The advanced characterization of the synthesized catalysts and the correlation of their properties with activity, selectivity and reaction mechanism were other objectives.

The separation and recyclability of the catalysts was designed to be achieved by the synthesis of a nanometric Fe_3O_4 magnetic core. The stabilization of this magnetic core was achieved by the encapsulation in a nanosize oxide layer. This structure represented the support for the heterogeneous catalyst.

In a first step, catalysts of the type X wt%Co@Nb_2O_5@Fe_3O_4 were prepared. Magnetic nanoparticles were encapsulated in a layer of niobium oxide (resulting the Nb_2O_5@Fe_3O_4 intermediate composite). On this composite, the cobalt was subsequently deposited resulting Xwt%Co@Nb_2O_5@Fe_3O_4 composites, which were subsequently reduced with hydrogen. The catalytic activity was explained by the concerted participation of niobium, catalyzing the acid hydrolysis of β-O-4 ' bonds and cobalt to cleave C-C bonds by hydrogenolysis. The optimization of the catalyst composition resulted in an optimal concentration of cobalt of 4wt%. For the reaction at 180° C and 10 atm H_2, this catalyst led to a conversion of 53% and a mixture of reaction products containing more than 96% C20-C28 and C29-C37 fragments. The investigated catalysts were re-used in six successive cycles of reactions. No leaching of the constituents has been detected by ICP-OES analysis [74].

The second class of investigated bifunctional catalysts was that of Re@Co@Nb_2O_5@Fe_3O_4 catalysts with metal concentrations ranging from 2 to 7 wt%. Magnetic nanoparticles were encapsulated by precipitation of the double oxalate of niobium and ammonium, in the presence of hexadecyl trimethylammonium bromide. Cobalt was deposited by precipitation-deposition, while the deposition of rhenium was performed by three methods: i) impregnation and ii) precipitation-deposition starting from rhenium chloride (V) (IMC and PP) and iii) impregnation starting from ammonium perrenate. On these bases, it has been determined that the preparation and the reduction influence the interactions that occuring between the Re and Co, the dispersion and the degree of the reduction of the metallic species. At the same time, it was pointed out that the increase in the acidity corresponds to a decrease in the degree of the reduction of the catalyst. Tests with the synthesized catalysts in the fragmentation of lignin confirmed the role of the structural and solvent characteristics.

The third category of investigated catalysts were the x% Re@SiO_2@Fe_3O_4 catalysts. The idea of investigating these catalysts was suggested by the catalysts X%Re@Y%Co@Nb_2O_5@Fe_3O_4, whose characterization showed that rhenium co-exists as both reduced (conferring the characteristics of a metal catalyst) and oxidized phase (conferring the characteristics of an acid catalyst) [93]. The acidity of rhenium is influenced by the metal – support interaction, and also by the dispersion of the active metal species [94]. The synthesis of these catalysts was accomplished by depositing rhenium on a magnetic core of Fe_3O_4 encapsulated in silica by two methods: impregnation and precipitation-deposition. Silica layer protects the magnetic nanoparticles during the deposition / reduction of rhenium onto the $SiO_2@Fe_3O_4$ material. The deposition of rhenium leads to the formation of catalysts with a high surface area containing mesopores in which rhenium is highly dispersed. As expected, rhenium was not reduced to the metallic state, part of it remaining oxidized with a week Bronsted acidity. This acidity was confirmed by the NH_3-TPD analysis. At the same time, H_2-TPD experiments have demonstrated the ability of these catalysts to chemisorb hydrogen, which confirms that rhenium has been reduced to an intermediate oxidation state. The catalytic fragmentation was carried out in the presence of water as a solvent. Under these conditions, it was observed that for the catalysts prepared by the PP method an advanced lignin fragmentation was obtained with high yields in the soluble / insoluble THF fractions, the highest yield being 98% for the 2% $Re@SiO_2@Fe_3O_4$ PP catalyst. The optimization of the lignin fragmentation process by changing the reaction parameters corresponded to an optimal temperature of 180° C, 10 bar hydrogen pressures and a reaction time of 6h. Another objective of this study was to verify the ability of the catalyst to fragment different types of lignin. Corroborating the structure of lignins, it has been determined that lignins containing a greater number of esteric bonds were more easy fragmented. Thus, the best results were obtained for lignins extracted by acid or Organosolv processes.

The above results represent a base for the study of the ability of this catalysts to deoxidize the lignin constituents. Starting from the premise that lignin is a phenolic copolymer resulting from the enzyme polymerization of sinapilic, coniferilic and cumaric alcohols [95,96] the aim of this study was to investigate the catalytic behavior of the catalysts synthesized in the deoxygenation of some model compounds. These reactions has been carried out under similar conditions to those in which different types of lignins have been fragmented. Another objective of this study was that of the acylation of lignin with octanoic acid in the presence of the same catalysts. The results obtained with both guaiacol and 3,4-dihydroxybenzaldehyde showed that the presence of rhenium favors repolimerization reactions, while the presence of cobalt inhibits this type of reaction to some extent.

In conclusion, these results confirmed the possibility of an advanced lignin fragmentation using recoverable and recyclable heterogeneous catalysts. In this way, this class of compounds can be produced without the need of use oil fractions. In addition, since the oxidation of hydrocarbon are still occurring with low selectivity, such an approach also has a pollution reduction effect, limiting the CO_2 emissions that result from the total hydrocarbon oxidation. Another important conclusion of this study is the identification of a simple type of catalyst ($Re@SiO_2@Fe_3O_4$), able to fragmentate lignins extracted from different species using water as solvent. The main disadvantage of the fragmentation of lignin is the production of a cocktail of products, which composition depends on the nature of the vegetal species from which the lignin was extracted, the production area, the climatic conditions, the extraction method, etc

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