The use of niobium compounds as catalyst in the production of biofuels: a review

Uso de compostos de nióbio como catalisadores na produção de biocombustíveis: uma revisão

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Resumo

A necessidade de substituir combustíveis fósseis por biocombustíveis não é um tema recente na comunidade acadêmica. Pesquisadores estudam e desenvolvem combustíveis alternativos há décadas e, com isso, combustíveis como o biodiesel e o etanol de primeira geração se consolidaram no mercado. No entanto, esses biocombustíveis de primeira geração competem com a indústria de alimentos, o que afeta sua oferta e preço. Por outro lado, os combustíveis de segunda geração são produzidos a partir de biomassa lignocelulósica e resíduos orgânicos de atividades urbanas e agroindustriais, não competindo com a indústria de alimentos. No entanto, a maioria desses processos ainda não é economicamente viável. Duas das principais contribuições para essa inviabilidade são o baixo desempenho dos processos (baixa conversão da matéria-prima e baixa seletividade dos produtos de interesse) e o alto custo dos catalisadores, que muitas vezes são feitos de metais nobres de pouca disponibilidade. O Nióbio é um metal com diversas aplicações, mas ainda pouco explorado industrialmente como catalisador, apesar de possuir propriedades interessantes para essa finalidade. Este artigo de revisão compila trabalhos envolvendo o uso do nióbio e seus

compostos como catalisador em diversos processos de produção de biocombustíveis, como esterificação, pirólise, liquefação, síntese Fischer-Tropsch, desoxigenação, entre outros. Além da revisão da literatura, este artigo apresenta uma análise crítica a respeito das aplicações de cada processo e tecnologia, bem como das pesquisas desenvolvidas pelos autores.

Palavras-chave: Nióbio. Biocombustíveis. Catálise. Biomassa. Desoxigenação. Pirólise.

Abstract

The need to replace fossil fuels with biofuels is not a fresh topic in the academic community. Researchers have been studying and developing alternative fuels for decades and, as a result, fuels such as biodiesel and first-generation ethanol have been consolidated on the market. However, these first-generation biofuels compete with the food industry, which affects their supply and price. On the other hand, second-generation fuels are produced from lignocellulosic biomass and organic waste from urban and agro-industrial activities, not competing with the food industry. Nevertheless, most of these processes are still economically unfeasible. Two of the main contributions to this unfeasibility are the low performance of the processes (low conversion of raw material and low selectivity of products of interest) and the high cost of catalysts, which are often made of noble metals of little availability. Niobium is a metal with several applications, but still little explored industrially as a catalyst, despite having interesting properties for this purpose. This review article compiles works involving the use of niobium and its compounds as a catalyst in various biofuel production processes, such as esterification, pyrolysis, liquefaction, Fischer-Tropsch synthesis, deoxygenation, among others. In addition to the literature review, this paper presents a critical analysis regarding the applications of each process and technology as well as the research developed by the authors.

Keywords: Niobium. Biofuels. Catalysis. Biomass. Deoxygenation. Pyrolysis.

1. Introduction

Biomass is the only sustainable source of organic carbon with the potential to reduce worldwide dependence on fossil fuels, in a scenario of increased energy demand, global warming, and greenhouse gas emissions (P. Wang et al., 2020). Currently, biodiesel and ethanol are the consolidated and commercially available biofuels. Although their use contributes to reducing CO_2 emissions, both fuels have limitations regarding their use in blends with fossil fuels due to the presence of oxygen in their compositions (Moreira et al., 2020). In addition, biodiesel and ethanol, as they are currently produced, are considered first-generation biofuels, which means that their production directly impacts the production and price of food, for using land for planting or inputs that could be used in food production (Havlík et al., 2011). On top of that, the industries in Brazil use methanol synthesized from non-renewable sources in the biodiesel production process for economic and technical reasons, even though the country is a large producer of ethanol from sugarcane.

Second-generation biofuels are produced from lignocellulosic biomass, agro-industrial waste, and organic urban waste. Consequently, its production does not impact the food market (Havlík et al., 2011). Second-generation biofuels production process is similar to the operation of an oil refinery in many ways. Thus, the concept of biorefinery emerges. What distinguishes the processes involving biorefineries from those present in oil refineries are the high concentration of oxygen and the different carbon chains. In the case of biorefineries, several thermochemical and catalytic processes have been studied for the treatment and upgrading of raw materials from renewable sources, aiming at the production of biofuels (Kang et al., 2020). Among them, we can mention the gasification and synthesis of Fischer-Tropsch and thermochemical processes such as pyrolysis and liquefaction followed by hydrodeoxygenation processes (Gollakota et al., 2018; Zuorro et al., 2020).

The employed catalyst is a fundamental factor for the viability of these processes. To produce hydrocarbons from lignocellulosic biomass, for example, it is necessary the cracking of natural

polymers (lignin, cellulose, and hemicellulose) and deoxygenation of cracking products. Cracking reactions are catalyzed by acidic sites on heterogeneous catalysts, while hydrogenation and deoxygenation reactions are catalyzed mainly by metallic sites (Moreira et al., 2020). Regarding that, tailored catalysts with these desired functionalities appear as alternative to perform different reactions simultaneously and to improve both yield selectivity of biofuel production processes. Niobium compounds may carry out these two steps simultaneously.

In this context, several niobium compounds have been studied as catalysts in the production of biofuels worldwide. This is due to their unique acidic and redox properties, and their stability (Kang et al., 2020). This review article presents several possibilities for the use of niobium in its various forms as a catalyst in the production of bioproducts, especially liquid biofuels.

2. Niobium

Niobium (Nb) is a rare, soft, ductile metal at ambient temperature. It has a high melting point (2468 °C) and good corrosion resistance (Grill & Gnadenberger, 2006). In its metallic form, niobium is grey, but it develops a bluish tinge if exposed to air for long periods (Alves & Coutinho, 2015). Niobium has great mechanical properties, being one of the lightest refractory metals, with a density of only 8.57 $g.cm^{-1}$, presenting a high strength-to-weight ratio, good tensile strength, and high elasticity modulus (Alves & Coutinho, 2015; Ayanda & Adekola, 2011).

Niobium has been applied as an alloying element, often in small proportions, to improve mechanical and chemical properties such as strength, corrosion resistance, superconductivity, heat resistance, and others (Bach, 2009; Nikishina et al., 2014). The most common use for Nb is in the manufacturing of high-strength low-alloy (HSLA) steel from Fe-Nb alloys, accounting for up to 90 % of total global production (Mackay & Simandl, 2014; Nikishina et al., 2014). These alloys, which usually contain 0.02–0.05 % Nb, are widely employed in applications requiring lighter and more resistant steels, such as in oil and gas pipelines, in platforms for oil exploration in deep waters, in the shipping industry, in the construction sector and in the auto industry (Alves & Coutinho, 2015; Bach, 2009). Niobium is also widely used in the composition of superalloys, materials designed to perform under high temperature applications, which are commonly used in nuclear reactor cores, rocket parts, and jet engine components (Alves & Coutinho, 2015; Bach, 2009). In recent years, however, great attention has been given to the application of niobium-based catalysts in processes to obtain biofuels (Gonçalves et al., 2011; Reguera et al., 2004; P. Wang et al., 2020).

2.1 Niobium in the world

More than 96% of all reserves of niobium are accumulated in pyrochlores ($[Ca,Na]_2Nb_2O_6[O,OH,F]$) and only 4% accumulate in columbites ($[Fe, Mn]Nb_2O_6$) and columbite-tantalites in granites, pegmatites, and placers (Mackay & Simandl, 2014). According to the 2017 Mineral Summary published by the Brazilian National Mining Agency, Brazil accounts for 93.1% of global niobium production and 98.8% of total niobium reserves (DNPM, 2017). Meanwhile, Canada holds shares of 6.7% and 1.2% of global niobium production and reserves respectively. Less representative Nb deposits can be found in Australia, Finland, Russia, among other countries (DNPM, 2017; Nikishina et al., 2014). The European Commission classifies niobium as a critical raw material considering its great importance for the modern economy and the strong dependence on new suppliers (EC, 2020).

Mine production and demand on niobium have increased greatly throughout the 21st century, mostly driven by infrastructural investments in emerging economies, among which China stands out (Alves & Coutinho, 2015; Mackay & Simandl, 2014). Global technological advancement also plays an important role in the growing niobium demand, given that many modern projects and processes require materials with increasingly noble properties. World mine production quickly escalated from 23,600 tons of Nb in 2000 to 63,000 tons in 2010, and once again to 97,000 tons in 2019. In the year 2020, due to the economical reflexes of the Sars-Cov-2 pandemic, niobium mine production retreated to 78,000 tons (*Mineral Commodity Summaries*, 2021; USGS, 2001, 2010,

2011).

2.2 Niobium in Brazil

Brazil is by far the world's greatest niobium producer and the owner of the largest Nb reserve. Mineable niobium reserves in Brazil are in the states of Minas Gerais, Amazonas, Goiás and Rondônia. In Minas Gerais, the main reserves, whose mining rights are held by the Brazilian Metallurgy and Mining Company (CBMM) are found in the city of Araxá, with a measured reserve of 742 Mt pyrochloride ore. In Goiás, the main reserves are in the cities of Catalão and Ouvidor, administered by China Molybdenum (CMOC), with a measured reserve of 82.3 Mt of pyrochlorine ore. In Amazonas, in the municipality of President Figueiredo, the Pitinga deposit stands out with a measured reserve of 108.2 Mt of columbite ore, while Rondônia's reserves are less significant. The mineral content varies on average from 0.21% to 2.85% of Nb_2O_5. Brazil exported 87% of its Fe-Nb alloy production in 2016, generating a US$ 1.3 billion revenue, while the other 13% was directed to the domestic market (Alves & Coutinho, 2015; DNPM, 2017; USGS, 2011).

Although very economically beneficial and crucial for the world's technological and infrastructural needs, Brazilian niobium mining has been raising some concerns regarding its environmental impact. A niobium Life Cycle Assessment has been the focus of a case study conducted in Brazil (Alves & Coutinho, 2019). The authors highlight the small product/waste ratio on Nb mining due to the low average niobium concentration on the ore. Therefore, an extremely strict waste management policy must be employed to mitigate the damage caused by the niobium mining and processing industries, especially due to the potential radiological hazard of the waste. A long-term prediction of non-processed waste radioactivity of the Catalão mine has been developed, and radiological hazard indices found were higher than the reference values or the global average (El Hajj et al., 2019). This fact raises some important concerns since the Brazilian authorities have shown special interest in Nb mining.

## 3. Niobium compounds catalysts and their properties

Niobium has been used in catalytic systems in the form of oxides, phosphates, and various modified formulations as support, as a promoter, or as the active phase (Guerrero-Pérez, 2020). In the last years, mainly due to their acidic and redox properties, the niobium-based catalysts have been studied for several different reactions, such as alcohol dehydration (Hilda Gomez Bernal et al., 2015; Catrinck et al., 2017; Gabriel et al., 2020; C. García-Sancho, Agirrezabal-Telleria, et al., 2014; C. García-Sancho, Rubio-Caballero, et al., 2014; Molina et al., 2015; Tirsoaga et al., 2021), hydrolysis (Campisi et al., 2018; Carniti et al., 2016; Catrinck et al., 2020; Maciel et al., 2020; Nogueira et al., 2020), oxidation (Cecchi et al., 2018; Chagas et al., 2013; Ding et al., 2020; Oliveira et al., 2012; Tran et al., 2019; Wasalathanthri et al., 2019; Wolski, 2020), esterification and transesterification (Câmara & Aranda, 2011; Deshmane et al., 2010; Cristina García-Sancho et al., 2011; Gonçalves et al., 2011; Hoekman et al., 2012; Miranda et al., 2011; Rezende et al., 2019; Singh et al., 2019), isomerization (Carniti et al., 2016; Kitano et al., 2012; Nogueira et al., 2020; Scaldaferri & Pasa, 2019a, 2019b; Wei et al., 2019), and photocatalytic reactions (Costa et al., 2020; Hashemzadeh et al., 2014; Moraes et al., 2020; Raba-Paéz et al., 2020). In the literature, the niobium compounds most used as catalysts are niobium pentoxide, niobic acid, and niobium phosphate.

3.1 Niobium Pentoxide and Niobic Acid

Niobium pentoxide (niobia - Nb_2O_5) and hydrated niobium oxide (niobic acid - $Nb_2O_5.nH_2O$) present remarkably strong acidic properties which are very interesting for catalytic applications (Nico et al., 2016). The acid character of niobium oxides is attributed to the presence of both Brønsted and Lewis sites. When compared to niobia, the hydrated niobium oxide presents superior acid properties, mainly due to the presence of protonic sites (Brønsted acid sites) generated by the incorporation of water molecules. On the other hand, Lewis acidity is related to the presence

of oxygen vacancies and structural flexibility of the system (Kreissl et al., 2017; Nowak & Ziolek, 1999). Regarding the structure of niobium oxides, the Brønsted acidity is associated with the presence of slightly distorted NbO_6 structures as well as NbO_7 and NbO_8 structures. Moreover, highly distorted NbO_6 octahedra, tetrahedral NbO_4, and NbO_5 sites are related to Lewis sites (Maurer, 1992; Nowak & Ziolek, 1999; Wachs et al., 2003). Additionally, previous studies have been showing that niobium oxides can maintain their acidic features even in the presence of water and, consequently, maintain their catalytic activity in aqueous systems or reactions with production of water (Dai et al., 2017; Nakajima et al., 2011; Omata & Nambu, 2020).

The final properties and the crystallization behaviour of niobium pentoxides are mainly dependents on the synthesis method and thermal treatments applied (Nico et al., 2016). The niobium pentoxide and niobic acid can exist in the amorphous phase but they start to crystalize at about 500 °C. Thermal treatment processes over 500 °C also result in the decreasing of acidic properties of these compounds, as a consequence of the decrease in the surface area and the transformation of Brønsted sites into Lewis sites due to the elimination of water molecules, as proposed in Figure 1 (Chai et al., 2007; Lebarbier et al., 2012; Nowak & Ziolek, 1999). Furthermore, these oxides generally present low surface area, being the mesoporous, nano-structured, and supported Nb_2O_5 materials an alternative to improve the morphological and surface properties (Cristina García-Sancho et al., 2011; Kang et al., 2020; Ziolek, 2003).
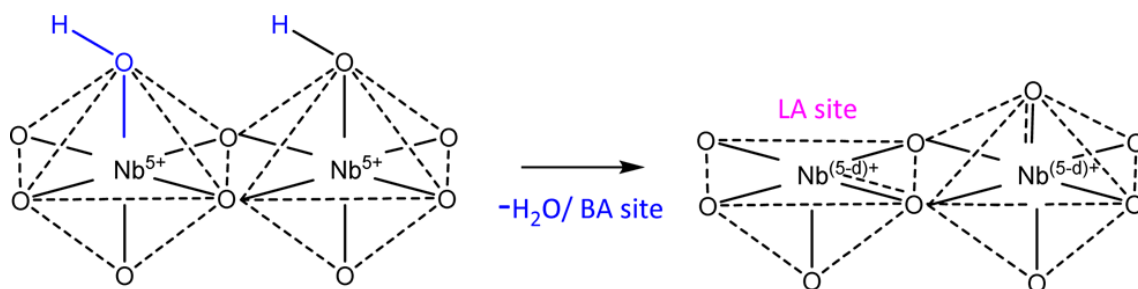

Figure 1 - Proposed oxygen vacancy/Lewis acid site formation via Brønsted acid site removal in the form of water. Reproduced with permission from ref. (Kreissl et al., 2017)**. Copyright (2020) American Chemical Society**

Another important characteristic of niobium pentoxide is its reducible character which makes it presents the SMSI (strong metal support interaction) effect, when used as support of transition metals. The SMSI can affect the catalytic performance by improving or worsening it due to geometric or electronic changes (Z. Chen et al., 1984; Nowak & Ziolek, 1999; Sousa et al., 2017).

3.2 Niobium Phosphate

The potential of transition metal phosphates to be applied in catalytic processes has been addressed in the literature (Lin & Ding, 2013). The niobium oxide phosphate, most known as niobium phosphate ($NbOPO_4$), has similar properties to niobium oxides, such as Brønsted and Lewis acidity, redox properties, and water tolerance. However, $NbOPO_4$ presents some advantages such as higher acid strength and better thermal stability, which enables the maintenance of its properties and amorphous character even after thermal treatments (Carniti et al., 2016; Florentino et al., 1992; Nowak & Ziolek, 1999).

Generally, niobium phosphate presents a lamellar structure, in which neutral layers composed of distorted NbO_6 octahedra connected by tetrahedral PO_4 are interacting by hydrogen bonding. The interlamellar space existing between the layers enables the occlusion of neutral molecules, such as water (Figure 2) (Reguera et al., 2004; Ziolek, 2003). The Brønsted acidity of niobium phosphate is associated with the presence of P-OH and Nb-OH groups. P-OH groups present stronger acidity when compared to Nb-OH, justifying the superior acid strength reported to $NbOPO_4$ when compared to niobium oxides. On the other hand, Lewis acidity is associated with the unsaturated Nb^{5+} sites (Hilda Gómez Bernal et al., 2019; Kang et al., 2020).
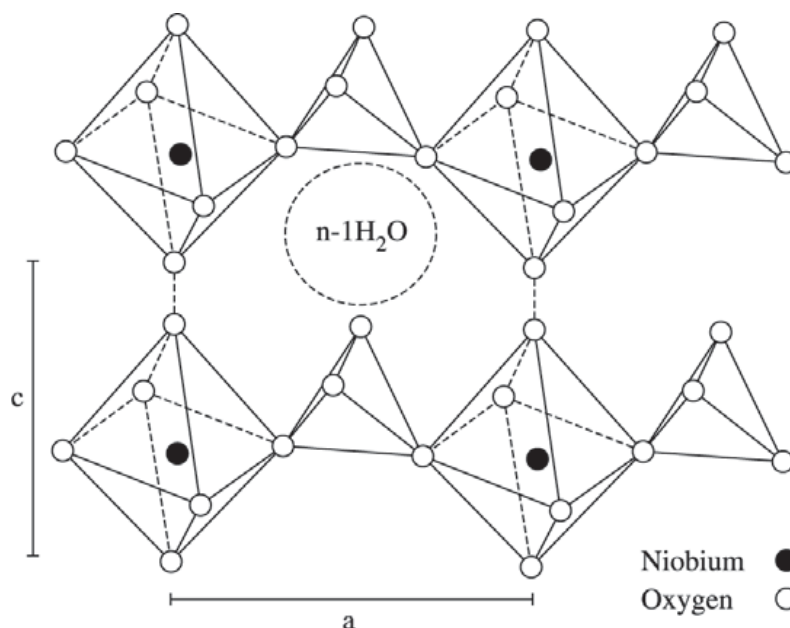
Figure 2 - Scheme of the lamellar structure of NbOPO$_4$.nH$_2$O on a plane. Reproduced from ref. (Reguera et al., 2004). (CC BY-NC 4.0).

4. Biofuels

In the following sections, the utilization of niobium compounds as catalysts in the production of several different types of biofuels is provided, including both first and second generations routes.

4.1 Biodiesel

Biodiesel, a worldwide-consolidated biofuel, has been sold in blends with petroleum diesel. It is a mixture of alkyl esters usually obtained by the transesterification of triacylglycerols, deriving from vegetable or residual oil or animal fat, with a short-chain alcohol in the presence of an alkaline or acid catalyst (Hoekman et al., 2012). Currently, the first-generation biodiesel is the most produced and commercialized, being obtained mainly from soybean and palm oils. Non-edible and microalgae oils can also be used as feedstock, resulting in second and third-generation biofuels, respectively (Singh et al., 2019). The alkaline transesterification reaction, which is the most used industrially, requires the use of noble triacylglycerols, with very low levels of water and free fatty acids. Otherwise, the saponification reaction takes place, consuming the catalyst and the raw material and making it difficult to purify the products (Gonçalves et al., 2011). To circumvent this limitation, it is possible to esterify acid oils using heterogeneous acid catalysts, as a preliminary step. Alternatively, the use of heterogeneous catalysts facilitates the recovery of the catalyst and its reuse (Cristina García-Sancho et al., 2011). Furthermore, biodiesel production via esterification is more flexible in terms of raw material purity but it is less used for economic reasons (Gonçalves et al., 2011).

Niobium-silicate molecular sieves were tested as catalysts in the production of biodiesel via transesterification of sunflower oil and methanol. The catalysts were produced from the impregnation of niobium oxalate in silica MCM-41 followed by calcination and by structural incorporation of niobium in silica MCM-41 during the synthesis stage. The results have shown a direct relation between the catalyst acidity and biodiesel yield. After 4 hours of reaction in a 12:1 methanol/oil molar ratio at 200 °C, a 95 % biodiesel yield was achieved over the catalyst produced from the impregnation of MCM-41 with 8 wt% of Nb$_2$O$_5$. Additional tests were performed with simulated degraded oils, prepared by mixing sunflower oil with different amounts of water and oleic acid. The results have shown that the presence of water has a negative effect on biodiesel production, whilst the presence of free fatty acids in concentrations up to 2.2 wt% did not affect considerably

the performance of the catalyst. Furthermore, the catalyst presented a great performance in the stability tests (Cristina García-Sancho et al., 2011).

Esterification reactions of free fatty acids were conducted using niobium oxide as a catalyst (79.8 wt% Nb_2O_5 and 19.6 wt% water; surface area of 180 $m^2.g^{-1}$). The reactions were carried out with anhydrous ethanol and 4 wt% hydrated ethanol in a 6:1 ethanol/free fatty acid and 20 wt% catalyst. The results indicated high conversions of stearic, palmitic, and lauric acids. Conversions from free fatty acids to alkyl esters at 200 °C with hydrated ethanol were between 78 to 84 %. Under the same conditions, conversions were between 73 and 77 % with anhydrous ethanol. The authors concluded that the influence of hydrated ethanol in the thermodynamic properties can be attributed to different dissociation constants of the carboxylic acids associated with stabilization of the carboxylic anion by water (Câmara & Aranda, 2011).

One of the disadvantages of biodiesel is its higher freezing point, which limits its application in cold climate regions. To improve the biodiesel performance at low temperatures, a mesoporous catalyst based on gallium and niobium (Ga-Nb) mixed oxide was synthesized, characterized, and tested in isomerization reactions of methyl oleate, one of the main components of biodiesel. Both gallium and niobium oxides have acid and redox activities, important properties for catalytic isomerization and dehydrogenation reactions, respectively. The batch reactions were conducted at 220 °C and autogenous pressures. The reaction produced molecules with methyl and ethyl branches, dehydrogenated diolefinic compounds, methyl palmitoleate, methyl palmitate, among other compounds, showing the isomerization and dehydrogenation activities of the tested catalysts. Oleic acid was also produced by the hydrolysis of methyl oleate due to the residual presence of water or surface hydroxyl groups (Deshmane et al., 2010).

There are also reports on the applications of niobium in the production of biodiesel via a biocatalytic process in the literature. Brazilian researchers have used *Candida rugosa* Lipase (CRL) immobilized in hydrated niobium oxide as a catalyst in the transesterification of babassu almond oil, a palm tree found in northeastern Brazil. The oil consists of 60-70 % saturated fatty acids, mainly lauric (C12) and miristic (C14). The authors have observed that the niobium oxide support played an important role by increasing the enzyme's thermal stability, according to results obtained by thermogravimetry. The transesterification reactions were carried out with ethanol, propanol, and butanol. Reasonable conversions (79.35 %) were observed only with butanol due to its lower polarity, which is responsible for maintain a minimum amount of water in the enzyme and, consequently, its catalytic activity (Miranda et al., 2011).

The effect of calcination temperature on niobium phosphate properties and catalytic performances was evaluated by Rade et al. (2019). Samples of commercial niobium phosphate were calcined at different temperatures (300, 350, 400, 450, 500, and 600 °C), characterized, and tested for esterification of oleic acid with ethanol in a continuous rector. Increasing the calcination temperature has promoted a decrease in surface area and acidity of $NbOPO_4$, as well as in the catalytic activity. However, it can be affirmed that niobium phosphate is thermally stable, mainly when compared to niobic acid, since its surface area and acidity have decreased considerably only after calcination at 600 °C. The catalyst prepared by calcination at 300 °C presented the best performance for esterification (250 °C, ethanol:oleic acid molar ratio of 6:1, 0.3 g of catalyst, and flow rate of 0.3 mL/min) due to its greater surface area, and higher acidity and thermal stability (Rade et al., 2019).

As mentioned before, alkaline homogeneous transesterification is the more consolidated route due to its technical and economic advantages. However, this route demands a raw material with low free fatty acids content (FFA), as well as low water content, proprieties often found in edible and noble oils, increasing the costs, and affecting the food market. In an approach to overcome this challenge, our research group developed a way to reduce the acidity of macauba oil by the re-esterification reaction between the free fatty acids and glycerol, in the presence of $NbOPO_4$. The use of an inorganic catalyst aims to reduce the reaction temperature, avoiding thermal degradation of the oil. A sample of macauba oil, with initial acidity of 43.90 wt%, was treated using excess glycerol (2:3 glycerol/FFA), 235 °C, with nitrogen flux, for 80 minutes. After the reaction, the

acidity was reduced to 0.8 wt%. The biodiesel produced using the treated oil, by alkaline homogeneous transesterification, presented high ester content (98.4 %) (Rezende et al., 2019).

In summary, niobium-based catalysts have been tested for biodiesel synthesis reactions, via acid esterification or transesterification, and have presented great potential for converting even non-edible oils with high acidity. Additionally, niobium compounds have been applied as catalysts in further reactions related to biodiesel production, such as isomerization and re-esterification, showing their versatility regarding different applications and types of reactions. Besides the conventional niobium oxide and niobium phosphate, novel niobium-based materials, such as mixed oxides and $Nb_2O_5.nH_2O$-supported enzymes, were proposed and open the way for developing more complex catalysts to be applied in further conversion routes.

4.2 Second-generation ethanol

Second-generation ethanol, which is produced from lignocellulosic biomass residue, is a promising alternative because, unlike its first-generation counterpart, its raw material does not compete with crops. However, the production route is more complex since pretreatment steps are necessary prior to the fermentation process (dos Santos et al., 2016). The first step consists of a structure modifying pretreatment, which enables the dissociation of the lignocellulosic complex, the reduction of its crystallinity, and the increase of the cellulose surface area, preparing the feedstock for the subsequent hydrolysis step. The hydrolysis is performed via an enzymatic route and produces the fermentable sugars (Haghighi Mood et al., 2013).

The structure modifying pretreatment technique depends both on the substrate composition and on the enzymatic hydrolysis step, which are related to the chosen enzyme and sugar release patterns. However, acidic pretreatment is the most used, as it has proven to be effective in a wide variety of lignocellulosic materials (Mosier, 2005).

The use of niobium pentoxide as an acid catalyst for *switchgrass* (*Panicum virgatum*) pretreatment was evaluated, given its acidic character. Pretreatment consisted of adding an amount of catalyst (0.25–1 g/g of switchgrass) in a solution of 6 g of biomass diluted in 90 ml of deionized water. The mixture underwent mechanical stirring (400 rpm) for predetermined times and temperatures. Then, it underwent enzymatic hydrolysis processes for 72 h and 168 h. The authors' objective was to measure hydrolysis conversion of glucan and xylan, which were present in lignocellulosic biomass pretreated with Nb_2O_5, into fermentable sugars, such as glucose and xylose. The highest glucose yields from glucan hydrolysis (77.51 %) were those of the switchgrass pretreated with 0.25 grams of catalyst per gram of biomass (120 min, 60 °C, 168 h reaction time). Maximum xylose conversion (28.9 %) was obtained from hydrolysis pretreated with 0.625 grams of catalyst per gram of biomass of pretreated (75 min, 60 °C, 72 h). Switchgrass treatment with niobium catalyst showed results comparable to other acid treatments concerning the conversion of glucose by enzymatic hydrolysis. Conversion to xylose, on the other hand, was below average. In addition, the Nb_2O_5 catalyst had good reusability, being used in four experiments without significant losses (Ansanay et al., 2014). Given that about 18 – 20 % of the total projected cost for the organic production of second-generation ethanol is attributed to the pretreatment stage (Haghighi Mood et al., 2013), the reusability of Nb_2O_5 has great potential for savings.

To the best of our knowledge, the work presented above is the only one in the literature describing the utilization of Nb-based compounds as catalysts in the lignocellulosic biomass pretreatment step. The results obtained and the common high performance of these compounds in acid-dependent reactions show that niobium catalysts have great potential to be used in the pretreatment steps of second-generation ethanol production. In this regard, it can be affirmed that there is a gap of studies about this utilization of niobium catalysts which can be addressed in future research.

4.3 Drop-in biofuels

Drop-in biofuels are liquid biohydrocarbons chemically similar to fossil fuels. This type of biofuels have the potential to fill the operational gaps left by the use of oxygenated fuels and can be used in existing structures, such as engines, turbines, and tanks, without the need for adaptations, in addition to being the only technically viable alternative to replace fossil aviation kerosene (Gutiérrez et al., 2017; Karatzos et al., 2017). Among the various processes reported and studied for the conversion of biomass into hydrocarbons, catalytic hydroprocessing can be highlighted. This process is one of the stages present in several of the drop-in biofuel synthesis routes, as shown in Figure 3 (Arun et al., 2015; Gutiérrez et al., 2017).
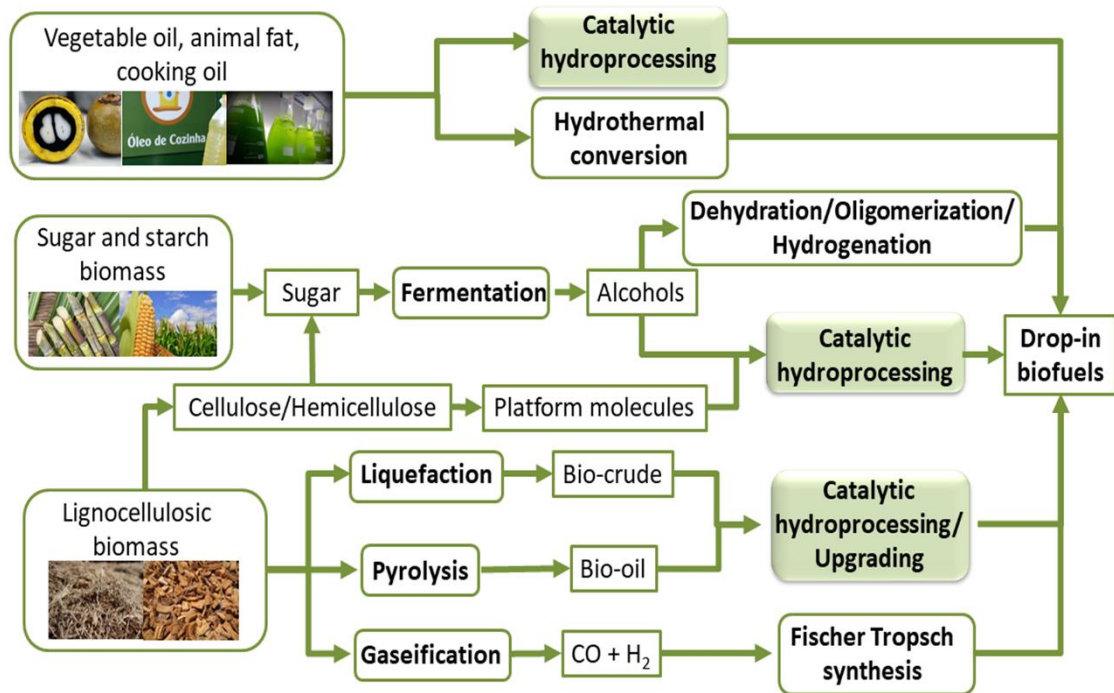
Figure 3 - Main drop-in biofuel production routes reported in the literature from different types of biomass.

The catalytic hydroprocessing comprises several reactions that allow the conversion of oxygenated compounds into hydrocarbons. This process is usually carried out at high temperatures (up to 350 °C), high H_2 pressures, and in the presence of a catalyst. The main reactions that occur during hydroprocessing are hydrogenation, deoxygenation, cracking, and isomerization reactions (Pattanaik & Misra, 2017). Specific catalytic sites, such as metallic, and/or hydrogenating, acidic and/or basic sites are required to catalyze the reactions described above. In this regard, the catalysts most used and studied in the production of drop-in biofuels are noble metals, transition metals, sulfides/carbides/nitrides/phosphides, and bifunctional catalysts containing metallic sites and acidic sites (Arun et al., 2015; S. Chen et al., 2019). In addition, approaches that reduce the H_2 dependence of the process have also been studied, in which the use of noble metal catalysts is less reported, giving rise to alternative catalysts (Rogers & Zheng, 2016).

Conversion of esters and fatty acids into hydrocarbons: Studies in the literature have reported the use of niobium compounds associated with noble and transition metals as catalysts in the synthesis of hydrocarbons from different fatty materials.

Transition and noble metals (Ir, Re, Pd, Pt, Cu, and Ni) supported on Nb_2O_5 were tested to obtain hydrocarbons (HCs) from the catalytic deoxygenation of lauric acid. The authors reported that Pt/Nb_2O_5 was the most active catalyst under the test conditions (8 bar H_2, 180 °C, 4 h), achieving

the highest conversion and yield of hydrocarbons. To understand the influence of support on catalytic activity, the authors tested Pt catalysts supported on other metal oxides and found that Pt/Nb_2O_5 had the best performance, proving the influence of niobium oxide on the final catalytic activity of the material. The catalyst characterization identified the presence of Lewis sites since the niobium oxide was treated at a temperature of 500 °C prior to the synthesis of the final catalyst. This thermic treatment enables the conversion of Brønsted acid sites into Lewis sites, by the dehydration of the oxide. The authors have proposed that the H_2 is dissociated on the platinum surface and the carbonyl group of the reactants is activated in the acidic sites of Lewis of the NbO_x species. Therefore the Pt/Nb_2O_5 catalyst's high efficiency on hydrodeoxygenation of fatty compounds was justified by the synergistic effect between the metal and the oxide (Kon et al., 2014).

Similar results were reported in a study on the activity of a palladium catalyst supported on $NbOPO_4$. Hydrodeoxygenation of palm oil and soy oil over $Pd/NbOPO_4$ (180 °C, 30 bar of H_2, and 24 h) resulted in 83.9 and 85.1 wt% of hydrocarbons in the diesel range, respectively. The catalyst characterizations after the reduction step showed the presence of Brønsted and Lewis acid sites. The strong Lewis acidity reported was attributed to the occurrence of reduction of the support, generating oxygen vacancies in its structure and exposing strong acidic Lewis sites (Nb^{+5}), which are capable of adsorbing and activating the triglyceride ester group. This characteristic combined with the ability of Pd to activate H_2 characterize a cooperative effect between the metallic and acidic sites of the catalyst, which is responsible for the high catalytic efficiency of $Pd/NbOPO_4$ for the hydrodeoxygenation of oils in mild conditions (Q. Xia et al., 2016).

The use of niobium compounds without the presence of additional metals as catalysts to produce hydrocarbons from esters and fatty acids has also been reported in the literature. Brazilian researchers tested the deoxygenation of oleic acid in the presence of three niobium-based catalysts: $NbOPO_4$ calcined at 623 K; Nb_2O_5, obtained from heat treatment of $H_8Nb_6O_{19}$ at 623 K; and H_3PO_4/Nb_2O_5, prepared by wet impregnation of a solution of H_3PO_4 in Nb_2O_5 support. Reactions were conducted in a continuous flow fixed bed reactor at atmospheric pressure under N_2 flow and 350 °C. Table 1 shows a summary of the characterizations of the three catalysts used. The greatest deoxygenations were obtained with $NbOPO_4$, with conversion up to 82 %. As can be observed in Table 2, the largest fraction of diesel was also obtained with the $NbOPO_4$. These results indicate that there is considerable difference in the catalytic properties of Nb_2O_5 and $NbOPO_4$, mainly related to the presence of strong acid sites, which were found in higher amounts in the $NbOPO_4$ sample (Reguera et al., 2004). In this regard, the strong acidity seems to have an important role in the deoxygenation reaction.

Table 1 - Properties of niobium-based catalysts (Reguera et al., 2004).

Catalyst	Surface area ($m^2.g^{-1}$)	Pore volume ($cm^3.g^{-1}$)	Average pore diameter (Å)	Total acidity ($\mu mol\ NH_3.g_{cat}^{-1}$)
$NbOPO_4$	119	0.31	71.0	143
Nb_2O_5	115	0.15	41.7	529
H_3PO_4/Nb_2O_5	78	0.13	51.5	811

Table 2 - Distribution of products expressed in the hydrocarbon range (Reguera et al., 2004).

Catalyst	C_6-C_{12} (Gasoline)	C_{14}-C_{18} (Diesel)	C_{19}-C_{22} (Lubricant)
No catalyst	-	-	-
$NbOPO_4$	0.72	33.12	65.12
Nb_2O_5	0.11	4.56	91.29
H_3PO_4/Nb_2O_5	1.77	21.32	72.79

The great catalytic performance of niobium phosphate was also reported by Scaldaferri et al. (2019), who has investigated the use of $NbOPO_4$ in the hydroprocessing of soybean oil. For the best

reaction conditions described in the work (10 bar H_2, 350 °C, and 5 h), the authors obtained 97 % yield in hydrocarbons, with high selectivity to linear and branched alkanes, cycloalkanes, and aromatic compounds. The authors attributed the occurrence of isomerization, cyclization, and aromatization reactions to the presence of Brønsted and Lewis acid sites in the $NbOPO_4$. The calcination of $NbOPO_4$ at low temperature (200 °C) enables the maintenance of Brønsted sites. Considering the importance of the presence of isoalkanes and aromatics in mixtures to be used as aviation biofuel, the product obtained in this work has the potential to be applied in aviation biokerosene formulations, as well as green diesel (Scaldaferri & Pasa, 2019a). In another work by the same research group, niobium phosphate performance for the production of alkanes from soybean oil in the absence of external hydrogen supply was studied and compared with other catalysts. Table 3 presents a summary of the results obtained in this work. The $NbOPO_4$ catalyst presented the best performance in the tested reaction conditions, with a high yield in linear and branched alkanes. The maximum content of hydrocarbons obtained in the liquid product was about 90 wt% for the 5 h batch reaction at 10 bar of N_2, 25 wt% catalyst and 350 °C. The product synthesized under these conditions presented a variety of hydrocarbons with carbon chains in the range of gasoline, kerosene, and green diesel. Regarding the great results presented, this process has a high potential for the production of drop-in biofuels from soybean oil, with the great advantage of using an inert gas instead of H_2 (Scaldaferri & Pasa, 2019b).

Table 3 - Liquid products yield and HC content in liquid products obtained from catalyst screening reactions (15 wt% catalyst, 10 bar N_2, 350 °C, 5 h, 500 rpm) (Scaldaferri & Pasa, 2019b).

| Catalyst	Liquid products yield (wt%)	HC content in liquid products (%)
No catalyst	83	47
$NbOPO_4$	91	86
FCC zeolite	88	68
HBeta zeolite	50	31
ZSM-5 zeolite	70	16
Pd/C	76	99

Considering the results presented so far, it can be concluded that the catalytic activity of niobium compounds for the deoxygenation of fatty compounds is directly associated with their acidic properties. Lewis acidity together with the catalytic properties of metals, such as Pd and Pt, characterizes a synergistic effect that favors the achievement of high yield and selectivity in hydrocarbons, even at low temperatures. The cooperation between the Brønsted and Lewis sites, on the other hand, seems to be responsible for the excellent catalytic performance of niobium phosphate without the addition of other metals, even in processes in the absence of H_2. However, there is a need for studies that go deeper into the characterization of the chemical properties of pure niobium phosphate and into the role of each property of this material during hydroprocessing reactions.

Conversion of lignocellulosic biomass derivatives into hydrocarbons: Lignocellulosic biomass is mainly composed of three biopolymers: lignin, cellulose, and hemicellulose. These biopolymers have chemical and structural differences between them, with lignin formed by phenylpropane units that are bonded mainly through ether and carbon-carbon bonds, while cellulose and hemicellulose are formed by simple sugars monomers. To be transformed into hydrocarbons with properties suitable for use as drop-in biofuels, these biopolymers need to undergo innumerable chemical processes composed of different reactions that generally are carried out in the presence of catalysts (Centi et al., 2011; F. Wang et al., 2021).

Xia et al. (2014) have studied the deoxygenation of furans obtained from aldolic condensation of furfurals using palladium supported on different supports as catalysts. From the catalytic tests with $Pd/NbOPO_4$, Pd/Al_2O_3, Pd/H-ZSM-5, Pd/Nb_2O_5, and with a physical mixture of Pd/Al_2O_3 with $NbOPO_4$, it was observed that catalysts with niobium had a better catalytic performance. The authors

obtained 100 % deoxygenated liquid product, composed of more than 90 % of octane, starting from furfural acetone and under mild conditions (170 °C, 2.0 MPa H_2) in a fixed bed reactor with a Pd/NbOPO$_4$ catalyst. The catalyst remained active for 256 h, with no reduction in catalytic activity. Considering the similarity between Pd/NbOPO$_4$ and Pd/Nb$_2$O$_5$ catalytic activities, the catalysts characterizations results, and the data obtained by the DFT calculations (Density Functional Theory), it was proposed that the NbO$_x$ species, present in both catalysts play an important role in breaking the C-O bond of the furan ring, accordingly to results reported in other studies presented in this review. Other products of the aldolic condensation of furfural and hydroxymethylfurfural with acetone also resulted in the production of alkanes from reactions with Pd/NbOPO$_4$ catalyst. The great results obtained can be explained by the oxophilic and acidic character of these niobium-based catalysts, which are responsible for the C-O cleavage and dehydration reactions, respectively (Q.-N. Xia et al., 2014).

In a later work by the same research group, the direct production of alkanes from furfural and 2-methylfuran (2-MF) was reported. It was developed a one-pot method with a Pd/NbOPO$_4$ multifunctional catalyst to perform simultaneously the following reactions: hydroalkylation/alkylation (HAA), condensation of furfural with 2-MF, and hydrodeoxygenation (HDO) (Figure 4). Initially, the authors studied the steps of HAA-condensation and HDO separately. A series of acid catalysts were tested for HAA-condensation, with niobium phosphate being the most active with a 97.4 % conversion to furfural, 96.5 % conversion to 2-MF, and 93.3 % yield in carbon, in the optimal conditions (80 °C, 5 h, and 2-MF/furfural ratio of 2.05). Furthermore, NbOPO$_4$ did not show a considerable loss in its catalytic activity even after five reuses in the optimal reaction conditions. For the HDO stage of HAA-condensation products, the authors compared the catalytic activities of metals Pd, Pt, Ru, and Ni, all supported in NbOPO$_4$, and reported the best results for the Pd/NbOPO$_4$ catalyst, with conversion and alkane yield of about 100 % (200 °C, 4 MPa of H_2, for 12 h). Unlike the reuse results obtained for the NbOPO$_4$ on the HAA reactions, Pd/NbOPO$_4$ catalyst presented considerable loss of catalytic activity after the fifth use in the HDO stage, due to the formation of carbon deposits on the catalyst surface. However, a catalyst regeneration step by calcination at 500 °C for 3 h resulted in the recovery of catalytic performance. From the results obtained for the HAA and HDO reactions done separately, the one-pot reaction was carried out in two stages. The first was carried out under the optimum conditions determined for the HAA-condensation and the second under the optimal conditions for HDO. From this method, the authors obtained a liquid product without the presence of oxygenated compounds and with an 89.1 % yield of alkanes in the diesel range (Q. Xia et al., 2017). Regarding its multifunctional character and the results presented so far, the Pd/NbOPO$_4$ catalyst appears to be a potential catalyst to perform sequential reactions to synthesize biohydrocarbons via the one-pot method from furfurals and furans.
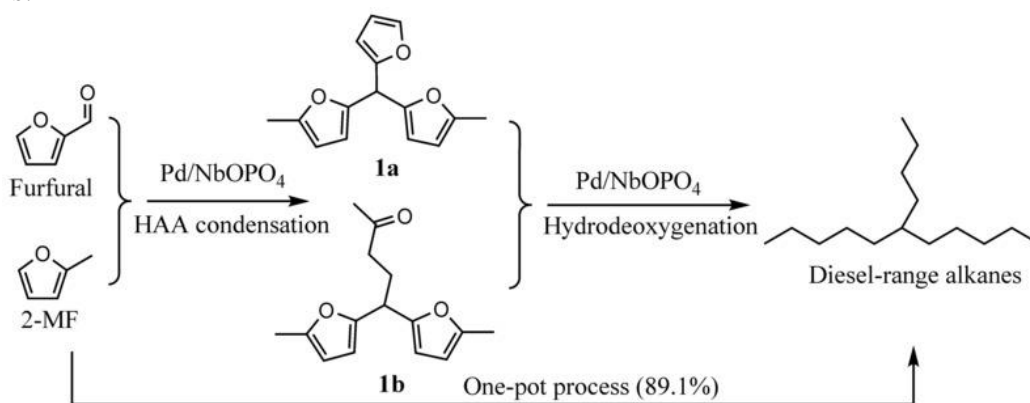
Figure 4 - Furfural/2-MF HAF reaction scheme followed by HDO of the formed furan intermediate (Q. Xia et al., 2017)**. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.**

In a similar approach, Samikannu et al. (2020) reported the synthesis and catalytic tests of a new acid catalyst of niobium phosphate dispersed in mesoporous silica (NbOPO$_4$/SBA-15) and a bifunctional catalyst with palladium (Pd/NbOPO$_4$/SBA-15). The objective was to obtain alkanes in the bio-jet fuel range from the conversion of furan compounds derived from biomass by a two-step process: hydro-alkylation/alkylation (HAA) and hydrodeoxygenation (HDO). From the results presented in Table 4, it is observed that the NbP-C/SBA-15 catalyst had superior activity and stability for the C-C coupling between 2-methylfuran and several carbonyl compounds, from the HAA reaction when compared to other conventional acid catalysts. In the tested reaction conditions, this catalyst had a 983 h^{-1} turnover frequency (TOF) and 92.6 % yield on HAA products. The authors justified the superior performance of this material based on its acidic characteristics, such as the greater ratio between the number of acidic Brønsted and Lewis sites and greater strength of the acidic sites, as well as from the uniform distribution and exposure of these acidic sites on the surface of mesoporous support (Samikannu et al., 2020).

Table 4 - Acid properties and reaction results of the catalysts tested for HAA (Samikannu et al., 2020)**.**

Catalyst	(M+S)/W[a]	B/L[b]	TOF (h^{-1})	HAA products yield (%)
NbP-D/SBA-15	3.42	0.63	462	94
NbP-C/SBA-15	11.6	1	983	92.6
NbP-B/SBA-15	4.05	0.95	510	85.8
NbP-A/SBA-15	3.42	0.48	434	83.1
Nb$_2$O$_5$/SBA-15	1.03	0.37	166	45.4
NbP-bulk	5.62	5.5	397	97
H-ZSM-5	1.16	-	18	3
Al-MCM-41	3.4	0.41	99	69
SiAl	4	-	25	22

[a] M = Medium sites; S = Strong sites; W = Weak sites; values determined by ammonia (NH$_3$)TPD.
[b] B = Brønsted sites; L = Lewis sites; values determined by the infrared results of the catalysts adsorbed with pyridine.

Tests for the HDO of HAA products over bifunctional catalysts with Pd also showed the potential of the synthesized materials to produce HCs from the furan adduct. Table 5 summarizes the results obtained from these reactions. Pd/NbOPO$_4$/SBA-15 catalysts had excellent performance, with 100 % conversion and up to 100 % hydrocarbon yield. For the HDO reaction, the authors concluded that the presence of medium/weak acid sites promoted the opening of the furan ring from the breakdown of the C-O bond more selectively, favoring the formation of branched HCs. On the other hand, the presence of strong Brønsted sites favored the simultaneous breaking of C-O and C-C bonds, producing lighter and linear compounds. In this sense, silica-supported niobium phosphate catalysts have adequate acidic and textural properties, resulting in an excellent catalytic performance for the tested reactions, being a potential alternative for the conversion of biomass into bio-jet fuel (Samikannu et al., 2020). Regarding the presented results, this work shows the potential of dispersing niobium-based compounds over supports as an approach to tailor and control the properties of the final material, such as acidity and morphology.

Many studies on the catalytic deoxygenation of phenolic monomers, compounds present in bio-oils derived from lignin, using catalysts with niobium compounds have been reported in the literature. Barrios et al. (2018) studied the activity of Pd catalysts supported on SiO$_2$ and Nb$_2$O$_5$ for the hydrodeoxygenation of phenol. The authors reported the superior performance of the Pd/Nb$_2$O$_5$ catalyst, which had a reaction rate up to 90 times higher than the Pd/SiO$_2$ catalyst, presenting greater selectivity to benzene. From the catalysts and products characterization results, it was explained that the greater selectivity for deoxygenated products obtained for Pd/Nb$_2$O$_5$ is due to the Nb^{4+}/Nb^{5+} oxophilic sites on the support. This characteristic guarantees a strong interaction between the Nb

cations with the phenol oxygen, favoring a reaction mechanism that furthers the hydrogenation of the phenyl tautomer carbonyl and dehydration of the alcohol formed, producing benzene. For the Pd/SiO_2 catalyst, the absence of the oxophilic character results in the preference for hydrogenation of the aromatic ring. The authors also concluded that, when reduced at high temperatures, the catalyst Pd/Nb_2O_5 presented a decrease in the catalytic activity. This decrease was explained by the formation of NbO_x particles covering the metal particles of Pd, characterizing the strong metal-support interaction (SMSI) (Barrios et al., 2018). These findings show how the properties of Nb_2O_5-supported metal particles catalysts can be affected by thermic treatments.

Table 5 - Conversions and yields obtained for the HDO reactions of the HAA product (2-methyl-5-(1-(5-methylfuran-2-yl) butyl) furan). Conditions: 50 mg of catalyst, 1.25 mmol of substrate, 3 ml of cyclohexane, 50 bar H_2, 200 °C, and 12 h (Samikannu et al., 2020).

Catalyst	Conversion (%)	Yield (%)		
		C14 HCs	**Total HCs**	**Oxygenated**
Pd/NbP-A/SBA-15	100	52.6	77.9	20.1
NbP-B/SBA-15	100	62.6	100	0
NbP-C/SBA-15	100	58.8	98.4	1.6
Pd/NbP-bulk	100	53.8	100	0
Pd/Nb2O5/SBA-15	100	32	35	65
Pd/H-ZSM-5	100	67.6	79.7	20.3
Pd/Al-MCM-41	100	68.8	73.3	26.7
Pd/C	100	0	0	100
Pd/SiAl	100	0	0	100

In another work by the same research group, performances of palladium catalysts supported on niobium oxide, niobium phosphate, and silica were studied for the hydrodeoxygenation of different model compounds, such as phenol, m-cresol, anisol, and guaiacol, as well as for the hydrodeoxygenation of a real substrate, the pinewood pyrolysis vapor. The reaction mechanisms for each catalyst and each molecule were described and discussed, as shown in Figure 5. It is demonstrated that the support and substrate functional groups influence the type of predominant mechanism. The authors reported that Pd/Nb_2O_5 catalyst had the greatest deoxygenation activity for all tested molecules. It was justified by its oxophilic character, and by the smaller size of catalyst metallic particles.

In addition, from the Pd/Nb_2O_5 stability study for phenol and guaiacol conversion, the authors observed a decrease in catalytic activity with an increase in reaction time. The catalyst deactivation occurred by the decrease in the metal dispersion and the accumulation of oxygenated intermediates adsorbed on the catalytic oxophilic surface. Based on the results of reactions with pyrolytic pine vapors, the authors highlighted the better performance of catalysts with niobium supports (Pd/Nb_2O_5 and $Pd/NbOPO_4$) on reducing the content of oxygenates even for real substrates (Teles et al., 2018).
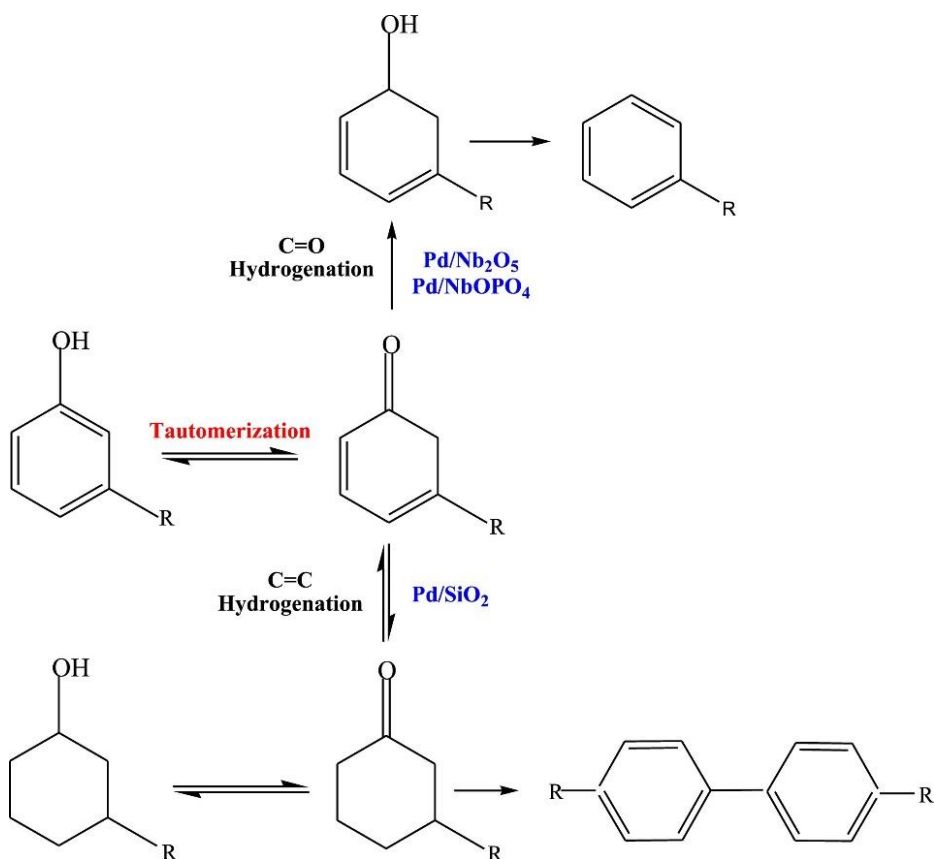
Figure 5 - Mechanisms of HDO reactions of substituted phenolic compounds on Pd catalysts supported on Nb$_2$O$_5$, NbOPO$_4$, and SiO$_2$. Reproduced from ref. (Teles et al., 2018)**. Copyright (2018), with permission from Elsevier.**

Niobium oxide and micro-mesoporous carbon (MC) composites supporting Ru catalysts were tested for phenol hydrodeoxygenation in a biphasic system using decaline and water as solvents under mild reaction. Under optimal reaction conditions (250 °C, 2 bar of H$_2$, Ru/5Nb$_2$O$_5$-5MC catalyst), the authors reported 100 % conversion of phenol and 80 % selectivity to benzene. The excellent catalytic performance was justified by synergistic effects between the Ru metallic particles, responsible for the hydrogenation/dehydrogenation reactions, and the Nb$_2$O$_5$-MC support acid and oxophilic sites. These sites are responsible for adsorbing the oxygenated compounds and activating the substrate's C-O bonds. Furthermore, the authors highlighted the importance of the amphiphilic character of composite support, which ensures emulsion stabilization of the biphasic system and, consequently, greater selectivity for benzene, since the presence of water in the system limits the occurrence of hydrogenation of the aromatic ring. Therefore, the use of the biphasic system and the proposed catalyst appears as a promising alternative for the valorization of lignin derivatives, from its conversion into hydrocarbons with potential for application as biofuels (C. Zhang et al., 2019).

Ma et al. (2019) studied the performance of Ru catalysts supported on different niobium materials to obtain hydrocarbons from the depolymerization and hydrodeoxygenation of lignin. The supports used were niobic acid, niobium phosphate, and layered niobium oxide. For reactions using lignin as a substrate (250 °C, 0.5 MPa of H$_2$, for 20 h) excellent results were obtained mainly for the Ru/Nb$_2$O$_5$-Layer catalyst, with 99.1 % molar yield in hydrocarbons and selectivity of 88.0 % in aromatic hydrocarbons. To understand better the network of reaction over the tested catalysts, the authors have performed additional experiments using the model compound *p*-cresol as substrate. The authors have concluded that the better performance of the Ru/Nb$_2$O$_5$-Layer catalysts to produce aromatics hydrocarbons is due to its higher density of Lewis acid sites and its lower metallic particle size (Ma et al., 2019).

The modification of a conventional carbon-supported Pt catalyst (Pt/C) with niobium using the Atomic Layer Deposition (ALD) method, resulting in a new catalyst (NbO$_x$ - Pt/C), has efficiently increased the selectivity towards toluene on *m*-cresol hydrodeoxygenation reaction. The authors reported that niobium modification on Pt/C catalyst increased process selectivity on toluene from 68 % to 95 %. From adsorption and spectroscopy studies using *m*-cresol and model catalysts, it was possible to conclude that the interaction at the interface between NbO$_x$ and Pt particles is responsible for stabilizing the Nb cations in a partially reduced state, which act as sites oxophilic for the adsorption of hydroxyl oxygen present in the substrate, as shown in Figure 6. The authors emphasized that this type of adsorption is different from that commonly reported for Pt catalysts, in which there is the adsorption of the aromatic ring with the metal surface, facilitating hydrogenation of the ring to produce saturated hydrocarbons. In this regard, it was concluded that the greater selectivity to toluene for the catalyst NbO$_x$ - Pt/C is justified mainly by the adsorption mechanism favored by this material, which induces C-O bond cleavage and hinders aromatic ring hydrogenation (T. Chen & Vohs, 2020).
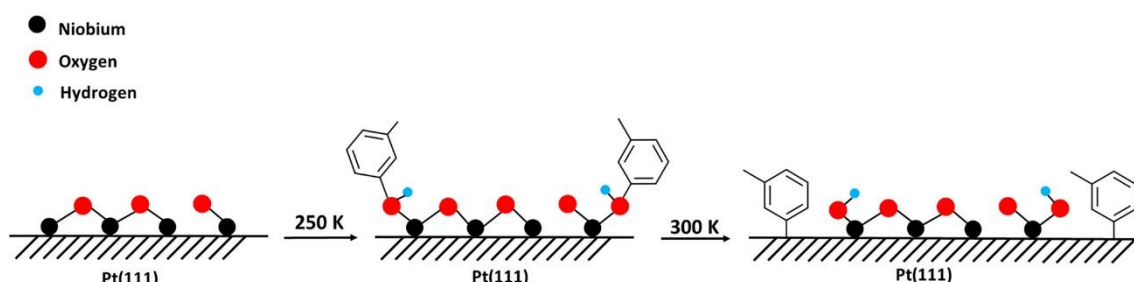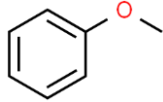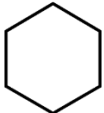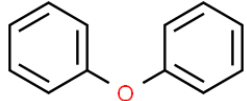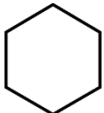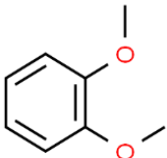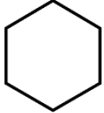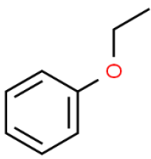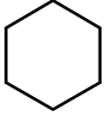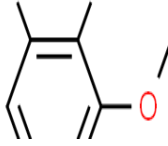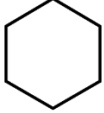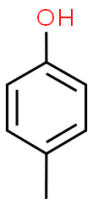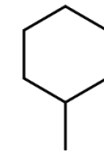

Figure 6 - Scheme of adsorption and reaction of m-cresol on the surface of NbO$_x$/Pt model catalyst. Reproduced with permission from ref. (T. Chen & Vohs, 2020)**. Copyright (2020) American Chemical Society.**

Ru catalysts supported on various materials containing niobium, such as phosphate and niobia, were also synthesized and tested for the production of cyclohexane from hydrodeoxygenation of anisole, in a dense and complete work developed by Zhao et al. (2020). Ru/NbOPO$_4$ catalyst had superior performance on initial catalytic tests (170 °C, 1 MPa of H$_2$, 2h of reaction), with 99.3 % conversion of anisole and 94.1 % selectivity in cyclohexane, indicating the high efficiency of this catalyst for deoxygenation even under mild reaction conditions. Regarding the catalysts characterization results, the authors attributed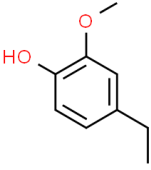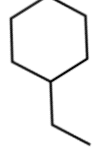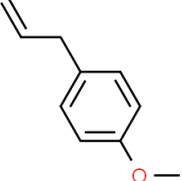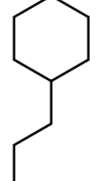 the greater activity of the Ru/NbOPO$_4$ catalyst to the presence of NbO$_4$ tetrahedral structures and distorted NbO$_6$ octahedrons, which act as Lewis acid sites and are responsible for methoxy group adsorption and CO bond activation. To evaluate the best activity of Ru/NbOPO$_4$ catalyst, catalytic tests were carried out using other model compounds, including ethers and aromatic phenols. The authors reported excellent catalytic performance of this material on lignin-derived compounds into HCs under reaction temperatures varying between 100 and 170 °C. Conversion and selectivity results are presented in Table 6 (H. Zhao et al., 2020).

Additionally, Ru/NbOPO$_4$ catalyst was tested for a real bio-oil upgrading (170 °C, 5 MPa H$_2$, 10 h), resulting in a reduction in oxygen content from 91.8 % to 6.9 % and an 88.2 % alkanes yield, confirming its great performance for this extremely complex substrate. The authors state that the excellent results obtained under mild conditions characterize the high potential of the Ru/NbOPO$_4$ catalyst for converting lignocellulosic biomass into liquid biofuels (H. Zhao et al., 2020). It is important to note that these results are different from those described in previously presented articles, in which materials with Nb$_2$O$_5$ had greater Lewis acid character and, consequently, greater selectivity for aromatic compounds. This observation indicates the great influence of catalysts preparation methods in their final properties.

Table 6 - Conversion and selectivity of HDO reactions with Ru/NbOPO₄ catalyst using different substrates (H. Zhao et al., 2020).

	Substrate	Temperature and reaction time	Conversion (%)	Main product	Main product selectivity (%)
1		170 °C, 2h 100 °C, 14h	99.3 97.1		94.1 93.7
2		170 °C, 2h 100 °C, 14h	94.8 94.0		98.8 74.5
3		170 °C, 3h 100 °C, 14h	99.4 94.9		84.2 61.7
4[a]		170 °C, 3h 100 °C, 15h	99.8 99.7		87.8 71.8
5		170 °C, 3h 120 °C, 14h	99.9 97.0		91.8 88.6
6		170 °C, 3h 120 °C, 14h	99.9 99.9		95.7 85.3
7		170 °C, 3h 120 °C, 14h	98.5 99.7		95.6 58.6
8[b]		170 °C, 3h 120 °C, 14h	99.7 93.6		95.0 70.7

Reactional conditions: 0.1 g of substrate, 0.1 g de solvent (decan), 1 MPa of H₂, dodecan internal standard
[a] Undecane was the solvent.
[b] Tridecane was the internal standard.

According to what was exposed in this item, it can be concluded that the niobium compounds used as catalysts for the conversion of different types of biomolecules have interesting properties and, consequently, excellent results for obtaining hydrocarbons. In general, the high catalytic performance of these materials is directly related to the acid properties of niobium materials. The balances between strong, medium, and weak acid sites and between Lewis and Brønsted sites are very important to develop versatile and suitable materials for each type of reaction, substrate, and desired product. Furthermore, Lewis acidity seems to be an important property to guarantee the conversion of phenolic compounds, by activating the C-O bond, and to improve the properties of the dispersed metallic particles.

Another trend research approach that has been reported in the literature as described above is the development of composite niobium-based materials. The association of niobium compounds with versatile materials widely used in the catalytic process such as silica and carbon materials is a promising way to control the chemical and morphological properties of the final catalyst, such as acidity, oxophilic character, and porosity. Therefore, this approach can result in very specific catalysts with desired activity, performance, and stability.

Fischer-Tropsc: Fischer-Tropsch (FT) reaction produces hydrocarbons from syngas (carbon monoxide and hydrogen) (Dry, 2002). This synthesis method is of great importance since it enables the production of liquid fuels from a feedstock that can be obtained from biomass through thermochemical processes, such as pyrolysis and gasification. For the FT reaction, obtaining high molecular weight hydrocarbons (C5+) is desired, while the production of large proportions of methane is indicative of a suboptimal process.

The FT reaction is typically catalyzed by iron or cobalt catalysts (Diehl & Khodakov, 2009). The catalyst active phase is usually supported on a porous oxide for mechanical and chemical stability. Niobia (Nb_2O_5)-supported cobalt catalyst has gained substantial interest due to its high selectivity towards C5+. Selectivity of 49 % has been reported on a FT synthesis under mild conditions (260 °C, 1 bar, 5 wt% Co, H_2/CO = 2) at which a C5+ product distribution of only 11 % was obtained by synthesis using alumina supported catalyst (Silva et al., 1993). The superior performance of Nb_2O_5 as a support material is attributed to its partial reduction and its strong interaction with cobalt, characterizing the SMSI effect (Mendes et al., 2006; Silva et al., 1993). Under high pressure conditions, Nb_2O_5 supported cobalt catalyst presented a C5+ selectivity of up to 90% (220 °C, 20 bar, 5 wt% Co, H_2/CO = 2) (den Otter & de Jong, 2014). In the same study, alumina-supported catalysts required four times more cobalt (25 wt%) to achieve comparable results in terms of CO conversion, proving the superior activity of cobalt when supported on Nb_2O_5. However, crystalline niobia presents a low porosity dense structure, which limits the maximum cobalt loading by impregnation. Multiple impregnations to obtain catalysts with cobalt content higher than 6 wt% usually result in larger cobalt particles, reducing the cobalt-niobia interaction and subsequently decreasing catalyst activity and C5+ selectivity (Hernández et al., 2017). In another study, to combine the positive C5+ selectivity of niobia with the high porosity of SiO_2, niobia-modified silica was prepared and applied as support for cobalt catalyst. Cobalt loadings up to 21 wt% were obtained, resulting again in a more active catalyst with no selectivity compromise (den Otter et al., 2016).

Fischer-Tropsch catalysts are often promoted with small amounts of noble metals and transition metal oxides to raise the reducibility and dispersion of the active phase particles, hinder catalyst deactivation, increase the number of hydrogen activation sites, and enhance the reactivity of active sites (Diehl & Khodakov, 2009). Niobium has been studied as a promoter for FT synthesis over Co/SiO_2 catalyst with great results (Huang et al., 2017). Huang et al. (2017) reported a considerable increase in CO conversion from 70.7 % to 94.1 % due to the promotion with a 1.57 wt% Nb loading. C5+ selectivity was also increased from 85.6 % to 89.1 %, while the catalyst activity increased 57 %. The presence of niobium as a promoter can significantly weaken the metal-support interaction, accelerating the reduction of cobalt oxides to a more active Co hexagonal close-packed phase (Huang et al., 2017, 2018). Furthermore, NbO_x species decreased BET average pore

volume, favoring a greater cobalt dispersion and promoting the formation of small cobalt particles. The effect of niobium promotion on iron and cobalt catalysts supported on carbon nanotubes has also been studied. For both active metals, the Nb loading with the best results was 0.4 wt%. In the iron-based catalysts experiments, Nb promotion resulted in a 38 % increase in CO conversion and a 67 % increase in C5+ selectivity, while increments of 62 % and 39 % were reported in the cobalt-based catalyst study on CO conversion and C5+ selectivity, respectively. Metal dispersion was enhanced in both studies by Nb promotion, while metal reducibility was increased only in the iron-based catalyst report (Ali et al., 2011, 2012).

In summary, we can conclude that the utilization of niobia (Nb_2O_5) as support or promoter in the Fischer-Tropsch process has been widely reported in the literature, presenting great performance and potential for improving conversion and C5+ selectivity. However, there is a lack of studies with further niobium compounds, such as niobium phosphate and novel Nb-modified materials.

4.4 Thermochemical processes for the production of bio-oil and biocrude

The thermochemical processes used in the production of biofuels are processes that use temperature and, in some cases, pressure to produce bio-oil or biocrude, biogas, and biochar from carbon-rich organic matter. The generated products can be used directly as an energy source or used as raw material for biofuel production. These processes do not require catalysts. But, many times, catalysts are used to improve selectivity or to improve some property of interest. This paper addresses pyrolysis, hydropyrolysis, and liquefaction processes.

Pyrolysis and hydropyrolysis: Pyrolysis is a thermochemical process that occurs in the absence of an oxidizing atmosphere upon heat, transforming the raw material (usually biomass) into biochar, bio-oil, and pyrolytic gas (F. Wang et al., 2021).

Chinese researchers studied the effects of Nb_2O_5 as a catalyst for fast pyrolysis of Enzyme Hydrolyzed Lignin (EHL), a by-product of the bioethanol industries that contains about 80 % lignin. The Nb_2O_5 was prepared using a modified hydrothermal method and had a greater distribution of the mesopores at 3.1 nm, a surface area of 113 $m^2.g^{-1}$, and a pore volume of 0.14 $cm^3.g^{-1}$. Furthermore, the catalyst presented Brønsted and, predominately, Lewis acid sites. To understand the Nb_2O_5 influence on pyrolysis products distribution, several catalyst/lignin ratios were studied, and it was observed that higher proportions of catalyst result in smaller amounts of oxygenated compounds and larger amounts of monocyclic aromatic hydrocarbons (94 % of formed hydrocarbons were aromatic). The temperature was another studied parameter (500 to 650 °C). The reaction conducted at a temperature of 650 °C and 9:1 catalyst/lignin ratio had the highest aromatic hydrocarbon yield. In addition to these observations, it has also been reported that higher proportions of Nb_2O_5 limit the number of solids and polycyclic aromatic hydrocarbons formed and, consequently, prevent the formation of char/coke over the catalyst. In summary, the authors concluded that niobia is a promising catalyst for fast-pyrolysis of high lignin content feedstocks for production of aromatic hydrocarbons (Li et al., 2020).

The influence of the utilization of two acid catalysts, zeolite ZSM-5 and niobic acid HY-340, on the pyrolysis of industrial Kraft lignins was studied and reported by Santana Junior et al. (2018). The results have shown that the utilization of both catalysts increased the hydrocarbons selectivity when compared to the pyrolysis with no catalyst. The use of ZSM-5 has promoted the formation of aromatic hydrocarbons while the niobic acid has produced mainly linear hydrocarbons, such as tetra and pentadecane. The major hydrocarbons selectivity was achieved using niobic acid, with a lignin-catalyst ratio of 1:10, at 550 °C, using the lignin type 1. The percentage area of hydrocarbons identified for this reaction was 92 %. The authors attributed the good performance of niobic acid to its already known capacity to favour the C-O bond cleavage and to its acid character, important characteristics to promote deoxygenation reactions (Santana et al., 2018).

The same catalysts, ZSM-5 and HY-340, were also tested in the hydropyrolysis of industrial Kraft lignins. Like conventional pyrolysis, hydropyrolysis is a process of thermal degradation but occurs in a reaction atmosphere moderately pressurized by hydrogen. The presence of hydrogen

inhibits the formation of undesirable aromatic polynuclear compounds, olefins, and free radicals, which normally are responsible for decrease the quality of the produced bio-oil. On the other hand, an efficient and stable catalyst for this process has yet to be developed and the high hydrogen consumption leads to high operating costs. The addition of niobic acid strongly influenced the increase in the hydrocarbons selectivity, whose maximum formation represented 93% of area (1:5 lignin-catalyst ratio, 650 °C), whilst during the non-catalytic hydropyrolysis of lignin there was no formation of hydrocarbons (Santana Junior et al., 2019). Therefore, we can affirm that, regarding that the difference between the selectivity of hydrocarbons between pyrolysis and hydropyrolysis using niobic acid as catalyst is negligible, the niobic acid present great performance even at inert atmosphere and is a potential catalyst to be used in the conversion of biomass into hydrocarbons in the absence of hydrogen.

Our research group has been working in the field of pyrolysis, mainly using urban solid residues as raw material. The pyrolyzes are performed in three different types of reactors: fixed bed reactor, continuous fluidized bed reactor, and solar slow pyrolizer. Up to now, the reactions were carried out without catalyst. However, regarding the potential and great catalytic performance presented by niobium composites in catalytic pyrolysis, the group intends to start the tests using them as catalysts, aiming for the simultaneous deoxygenation of the products.

Liquefaction: Biomass liquefaction has been studied since the 1920s and, in recent years, the scientific interest about it has impressively grown due to environmental issues (Hou et al., 2021). Liquefaction can be seen as a combination of pyrolysis and hydrolysis processes since it combines thermal chemistry and the utilization of a liquid solvent under temperatures between 200-400 °C. It depolymerizes, cracks, and partially deoxygenates the lignocellulosic material producing the biocrude, a complex organic liquid, that can be converted into biofuels by a catalytic upgrading process (Lange, 2018). When the solvent used is water, the process is known as hydrothermal liquefaction, an interesting alternative for the conversion of biomasses with higher water content, such as microalgae (S. Zhang et al., 2019).

Even though the liquefaction process does not necessarily require the use of a catalyst, the current focus of liquefaction research is on the utilization of catalysts able to improve the biocrude yields and to perform deoxygenation/upgrading reactions simultaneously (Scarsella et al., 2020). This objective can be achieved by applying acid-base catalysis, which can perform depolymerization and hydrolysis reactions, and also metallic catalysts, which can perform the biocrude deoxygenation, such as has been reported in the literature (Araújo et al., 2020; Duan & Savage, 2011; Govindasamy et al., 2019; J. Zhang et al., 2013; B. Zhao et al., 2021).

Xia et al. (2016) have published interesting work on the conversion of wood sawdust into alkanes over a multifunctional $Pt/NbOPO_4$ catalyst under mild conditions (190 °C, 5 MPa H_2, 20 h) using cyclohexane as solvent. The catalyst was able to depolymerize the lignocellulosic complex and convert cellulose, hemicellulose, and even the lignin fractions into hexane, pentane, and alkyl cyclohexanes, respectively, and to achieve yields up to 28.1 wt% of alkanes in a one-pot process. From additional experiments performed with other catalysts and with model molecules, the authors justified the superior performance of $Pt/NbOPO_4$ based on the synergistic effect between Pt, NbO_x species, and the Brønsted and Lewis acidic sites on the support. The NbO_x sites combined with acid properties were capable to promote C-O bond cleavage and the hydrogenolysis of C-O-C ether bond of lignin. Furthermore, stability tests were also performed showing the good recyclability and stability of the catalyst. Hence the presented one-pot process over $Pt/NbOPO_4$ catalyst seems to be a potential alternative for biofuels production from raw biomass (T. Chen & Vohs, 2020).

The same research group has published another work reporting the hydrothermal liquefaction of lignin into arenes over a Ru/Nb_2O_5 catalyst. Several catalysts (Ru/Nb_2O_5, Ru/ZrO_2, Ru/Al_2O_3, Ru/TiO_2, $Ru/HZSM-5$, and Ru/C) were tested for the lignin liquefaction (0.1 g lignin, 0.2 g catalyst, 15 mL water, 250 °C, 0.7 MPa H_2, 20 h). The Ru/Nb_2O_5 catalyst presented the best performance, with a near-quantitative carbon yield, with total mass yield of 35.5 wt% for liquid hydrocarbons, and monoaromatics hydrocarbons selectivity of 71 wt%. The authors have shown that the proposed

catalyst could perform the depolymerization of lignin followed by hydrodeoxygenation, via the cleavage of $C_{aromatic}$-OH bonds, which is a hardly achieved mechanism and is responsible for the direct production of arenes from phenolic monomers over the Ru/Nb_2O_5 catalyst. From the results obtained by inelastic neutron scattering (INS) and density functional theory (DFT) calculations, the authors have concluded that the dissociation energy for $C_{aromatic}$-OH bonds in phenolics is significantly decreased upon adsorption on the Ru/Nb_2O_5 catalyst, justifying its unique catalytic performance and selectivity to arenes (Figure 7). In summary, the authors claim that the proposed hydrothermal liquefaction of lignin over Ru/Nb_2O_5 is a promising approach for the production of valuable aromatic hydrocarbons (Shao et al., 2017).
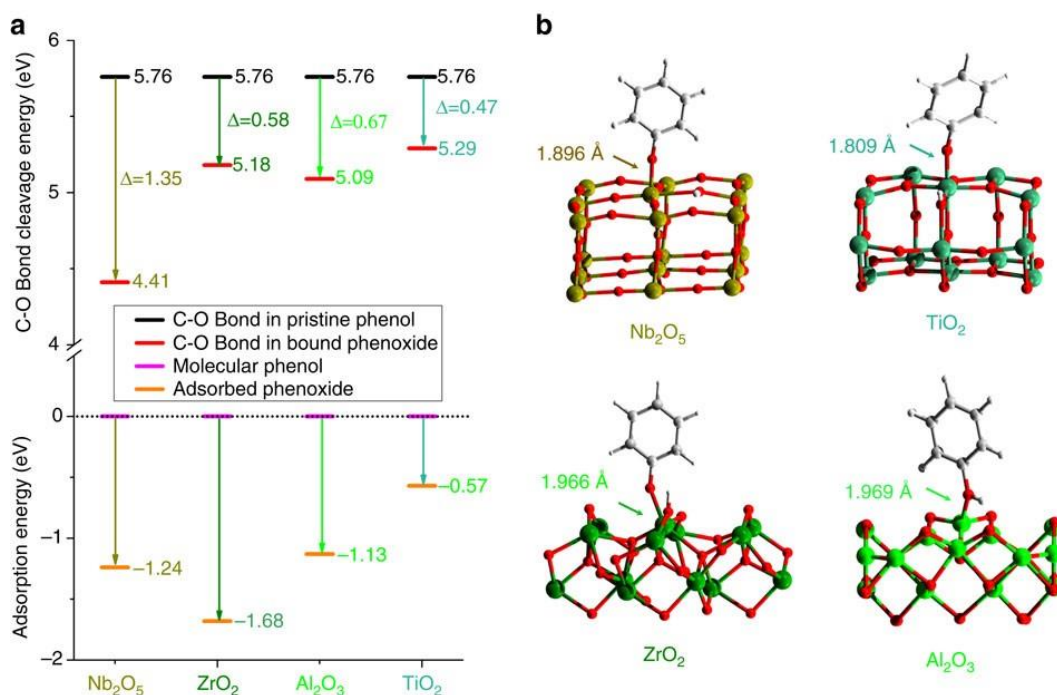
Figure 7 - (a) Calculated energies for phenol adsorption (that is, a combination of deprotonation of $C_{aromatic}$–OH to form phenoxide bound to the vacant surface metal sites and the formation of surface –OH groups) and disassociation of the C–O bonds upon adsorption over Nb_2O_5, ZrO_2, Al_2O_3 and TiO_2. (b) Views of the corresponding DFT-optimized structural models for the phenoxide bound on $Nb_2O_5(001)$, $ZrO_2(010)$, $Al2O_3(110)$ and $TiO_2(101)$ surfaces. Reproduced from ref. (Shao et al., 2017) **(CC BY 4.0).**

In the light of the above and considering their general properties and great catalytic performance, niobium compounds appear as an interesting option for further studies to fill the gap on the use of heterogeneous catalysts in the liquefaction route. Our research group has been studying the lignocellulosic biomass liquefaction process to obtain biopolyols for the synthesis of polymers, especially polyurethanes. The lignin, crude glycerol, castor oil, liquid from the cashew nut bark, curauá fiber (*Ananas erectifolius*), and pulp and endocarp of the macauba have already been studied to obtain biopolyols to synthesize foams and polyurethane coatings. In these studies, biomass liquefaction occurred from solvolysis reactions by polyhydric alcohols using acid catalysis, which showed good results. Mainly due to its acid character, niobium composites will be tested in future studies.

5. Conclusion

Herein we have provided a dense overview of the utilization of niobium compounds as catalysts in several conversion processes for the production of biofuels. The utilization of niobium-based catalysts was proposed for the conversion of different types of raw materials, such as vegetable oils, lignocellulosic biomasses, renewable platform molecules, and residual feedstocks, through different processes into several types of biofuels, such as biodiesel, second-generation ethanol, and drop-in biofuels.

In summary, the conversion routes over niobium-containing catalysts have much potential to be applied in the production of biofuels, since the great majority of the works about it have obtained outstanding results. It can be concluded that the excellent catalytic performance of niobium catalysts is most related to their unique physical-chemical properties and versatility. They generally present redox and acid properties, with both Brønsted and Lewis sites. The Lewis acidity is mainly related to the presence of unsaturated niobium cations that acts as oxophilic sites and favours the adsorption and activation of C-O bonds, which are one of the main linkages presented in the lignocellulosic complex and in other biomass-derived compounds. Moreover, the versatility of niobium catalysts lays down in the dependence of their properties on the precursor and methods applied during their synthesis and also on the used thermal pretreatments. Hence it is possible to tailor the desired properties to the final catalyst, such as acidity, crystallinity, and surface properties based on the synthesis methods.

The most reported niobium-containing compounds were the niobium pentoxide, also known as niobia (Nb_2O_5), the hydrated niobium pentoxide, most called niobic acid ($Nb_2O_5.nH_2O$), and the niobium phosphate ($NbOPO_4$). Further niobium-based compounds were also tested for catalytic production of biofuels, such as modified or mixed oxides and composites, and their development seems to be a promising approach to synthesize tailored catalysts with distinct properties. The utilization of niobium materials associated with transition metals, resulting in multifunctional catalysts, was also very reported and presented excellent performance which was mainly associated with synergistic effects between the metallic sites and the acid sites.

Furthermore, the niobium has been standing out mainly when used in the production of biohydrocarbons, the so-called drop-in biofuels. Several works, mainly related to the deoxygenation of phenolic model compounds and the upgrading of raw bio-oils, were reported here, with outstanding selectivity to desired alkanes. In the case of deoxygenation of lignocellulosic-derived compounds, the role of the niobium compounds as catalysts was largely discussed based on the results of several different reactions, characterization techniques, and theoretical methods. Further conversion routes, such as pyrolysis and liquefaction, were also performed over niobium materials but on a smaller amount, despite the great results obtained with niobium compounds-supported noble metals mainly for liquefaction reactions.

In the light of the above, we can highlight some opportunities to develop further works with niobium-based catalysts, as following:

1. The development of tailored niobium composites with unambiguous properties to be applied in very specific processes or reactions;
2. More studies with niobium catalysts in the pretreatment steps of second-generation ethanol production, in a way to improve the results obtained so far;
3. More detailed studies about the application of niobium catalysts in the deoxygenation of fatty compounds in inert atmosphere, considering the great results presented in previous works;
4. Studies about the application in large scale and with real substrates of the proposed process for conversion of lignocellulosic derived compounds into hydrocarbons over the niobium-based catalysts;
5. More studies about thermochemical processes for conversion of solid biomass into liquids alkanes, such as pyrolysis and liquefaction, over different niobium-based catalysts and using

different types of feedstocks. In the case of the liquefaction route, to understand better the relation between types of solvents and the catalyst used. In addition, studies to check if the processes are scalable and industrially viable.

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