

Niobium Pentoxide as an Acid Catalyst: An Overview

O Pentóxido de nióbio como catalisador ácido: Uma visão geral

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Abstract

The global chemical industry is under increasing pressure to adopt more sustainable practices, as most chemical products exceed environmental safety limits. Given that chemical production largely relies on catalytic processes, the development of solid acid catalysts has become crucial for more sustainable production. Among these catalysts, niobium pentoxide (Nb_2O_5) stands out due to its strong acid sites, which remain active in the presence of water, and its stability under hydrothermal conditions. Recent studies have demonstrated that these solids maintain their catalytic activity even in the presence of strong bases, making them unique catalysts. This review explores the potential of Nb_2O_5 as an acid catalyst, addressing advances in synthesis techniques, surface modifications, and combinations with other materials to enhance its catalytic performance in sustainable applications, such as biomass conversion and biofuel production, opening new pathways for the production of greener chemicals. Finally, the future perspectives of Nb_2O_5 -based catalysts in green chemistry are discussed.

Keywords: heterogeneous catalysis. acidic solids. niobium oxides. niobium pentoxide.

Resumo

A indústria química global está sob crescente pressão para adotar práticas mais sustentáveis, uma vez que a maioria dos produtos químicos excede os limites de segurança ambiental. Dado que a produção química depende amplamente de processos catalíticos, o desenvolvimento de catalisadores ácidos sólidos tornou-se crucial para uma produção mais sustentável. Entre esses catalisadores, o pentóxido de nióbio (Nb_2O_5) se destaca por seus fortes sítios ácidos, que permanecem ativos na presença de água, e por sua estabilidade em condições hidrotérmicas. Estudos recentes demonstraram que esses sólidos mantêm sua atividade catalítica mesmo na presença de bases fortes, tornando-os catalisadores únicos. Esta revisão explora o potencial do Nb_2O_5 como catalisador ácido, abordando os avanços em técnicas de síntese, modificações de superfície e

combinações com outros materiais para aprimorar seu desempenho catalítico em aplicações sustentáveis, como a conversão de biomassa e a produção de biocombustíveis, abrindo novos caminhos para a produção de produtos químicos mais ecológicos. Por fim, discutem-se as perspectivas futuras dos catalisadores à base de Nb_2O_5 na química verde.

Palavras-chave: Catálise Heterogênea. Sólidos Ácidos; Óxidos de Nióbio, Pentóxido de Nióbio.

1. Introduction.

In 2022, the global chemical industry generated \$5.72 trillion in revenue, with an estimated growth of 1.8% projected for 2024 (Statista, 2024). An Absolute Environmental Sustainability Assessment (AESAs), based on the Planetary Boundaries framework, analyzed the production of 492 chemical products and revealed that about 99% of them exceed safe environmental limits, particularly regarding greenhouse gas emissions, including climate change, ocean acidification, and loss of biosphere integrity (Tulus *et al.*, 2021). This scenario highlights the challenge facing the chemical industry: implementing more sustainable production standards without compromising its competitiveness in the global market.

It is estimated that 85% of the chemical industry's production depends on catalytic processes (De Jong, 2009). Heterogeneous catalysis is a cornerstone for manufacturing chemicals via more sustainable routes (Mitchell *et al.*, 2024). The replacement of liquid acids with solid acid catalysts, which exhibit high catalytic activity, has garnered significant interest in green chemistry and is widely applied in sectors such as petroleum refining and chemical synthesis (Hita *et al.*, 2024; Mansir *et al.*, 2017; Mitchell *et al.*, 2024).

The expectation is that solid acid catalysts will play a key role in the development of sustainable chemical processes, such as the conversion of renewable biomass into chemicals and fuels (Kang *et al.*, 2021; Mansir *et al.*, 2017; Moreira *et al.*, 2022; Munyentwali *et al.*, 2022; Tian *et al.*, 2021). One of the main challenges for these materials is their ability to operate in the presence of water under hydrothermal conditions. In this context, niobium oxides emerge as a promising alternative, as they demonstrate water tolerance and maintain catalytic activity in various solvents (Armaroli *et al.*, 2000; Carniti *et al.*, 2008; Omata *et al.*, 2020). Recent studies indicate that these catalysts exhibit remarkable resistance to basic inhibitors, such as amines and water, in nucleophilic substitution reactions of carboxylic acids and their derivatives, broadening their range of applications (Ali *et al.*, 2015; Ali *et al.*, 2016; Ali *et al.*, 2014; Hirunsit *et al.*, 2018; Siddiki *et al.*, 2019).

Niobium exhibits oxidation states ranging from +5 to -1, with +5 being the most stable (Nico *et al.*, 2016). Currently, Brazil holds about 98% of the world's niobium reserves, followed by Canada with 1.5% and Australia with 0.5%. Additionally, Brazil is the world's largest producer of niobium, accounting for 90% of global production (Williams-Jones *et al.*, 2023). Given the abundant availability of this material, it is evident that further studies exploring new technological applications, thereby adding value to niobium and its compounds, are essential.

Niobium oxides have been intensively investigated in recent years due to their unique chemical properties, which are explored across various fields (Antunes *et al.*, 2024; Gireeshkumar *et al.*, 2023; Santos *et al.*, 2019; Ma *et al.*, 2020; Nunes *et al.*, 2020; Silva *et al.*, 2020; Talukdar *et al.*, 2023; Wu *et al.*, 2022; Yi *et al.*, 2021; Yu *et al.*, 2024; Zhou *et al.*, 2020). These solids can form a complex system with several interesting polymorphic phases (Hidde *et al.*, 2019). There is a wide variety of niobium oxides with different structural formulas, such as NbO_x . They can exist in various stoichiometries, including niobium pentoxide (Nb_2O_5), niobium dioxide (NbO_2), and niobium monoxide (NbO), and can also be found as anions in ternary oxides, such as KNbO_3 , NaNbO_3 , and LiNbO_3 (Ma *et al.*, 2020). Niobium oxides also exhibit non-stoichiometric, metastable, and mixed phases, making the Nb–O systems highly complex and challenging to study.

This review focuses on niobium pentoxide (Nb_2O_5), its most stable and well-known form, which is a white, non-toxic solid, air-stable, and insoluble in water. Nb_2O_5 is significantly more resistant to reduction compared to vanadium oxide, which belongs to the same group V of the periodic table (Ding *et al.*, 2023). Nb_2O_5 contains Brønsted and Lewis acid sites (Vieira *et al.*, 2020), exhibiting high acidity and amphoteric characteristics, capable of dissolving in both strong acids and strong bases. Its crystalline structure generally consists of NbO_6 octahedra, which can present different degrees of distortion. The structural complexity of Nb_2O_5 is influenced by synthesis methods and variables (Fuchigami *et al.*, 2020).

Niobium pentoxide exhibits a considerable surface area, high catalytic activity, and selectivity due to the presence of strong acid sites on its surface (Andrade *et al.*, 2014), making it successfully used as a catalyst in alkylation (Pineda *et al.*, 2020), dehydration (Ghosh *et al.*, 2019), esterification (Bassan *et al.*, 2013), biofuel production (Chhabra *et al.*, 2023; Hosseinzadeh-Bandbafha *et al.*, 2018), biodiesel byproduct valorization (Souza, *et al.*, 2015), and glucose dehydration (Eblagon *et al.*, 2020), among others. Niobium oxides also demonstrate other interesting chemical properties for catalysis, such as redox capability (Wada *et al.*, 1990; Ziolek *et al.*, 2011) and photosensitivity (Rozina *et al.*, 2024; Wu *et al.*, 2022).

In addition to the synthesis method, factors such as morphology (Ali *et al.*, 2017; Fuchigami *et al.*, 2020; Kreissl *et al.*, 2017; Marin *et al.*, 2014; Zhang *et al.*, 2020) and the dispersion of niobium pentoxide on other surfaces (Carniti *et al.*, 2008; Ferreira *et al.*, 2018; Prasetyoko *et al.*, 2008) have proven to be promising alternatives for obtaining new acid catalysts. This potential can be further explored through chemical treatments that incorporate new active sites (Bassan *et al.*, 2013; Eblagon *et al.*, 2023; Ghosh *et al.*, 2019; Liu *et al.*, 2023) or by incorporating organic molecules that modify the hydrophilic character of these materials (Padula *et al.*, 2018; Souza *et al.*, 2014; Souza *et al.*, 2015), as well as through combinations with other materials, such as silicates (Antunes *et al.*, 2024; Pineda *et al.*, 2020), phyllosilicates (Oliveira *et al.*, 2024), and carbonaceous materials (Saadaoui *et al.*, 2023). Another relevant property of niobium oxides is their peculiar catalytic activity in the presence of water, which has been the focus of recent studies (Dai *et al.*, 2017; Omata *et al.*, 2020).

In the following sections, general comments will be presented on the most used techniques for characterizing the acidity of solid surfaces, as well as an introduction to the basic structures of niobium oxides. Next, recent studies in the literature dedicated to obtaining niobium pentoxides as more efficient acid catalysts will be addressed. This review aims to provide an overview of how the acid sites of niobium pentoxide operate and how modifications to the structure and surface of these oxides can influence the behavior of active acid sites in various reactions. Finally, this review will conclude with final considerations and future perspectives.

2. Solid Surface Acidity - Characterization Techniques

Acidity is a fundamental chemical property that will guide the discussions in this review. Information such as the type of acidity (Brønsted and Lewis), its strength, concentration, and distribution play crucial roles in the activity and selectivity of catalytic reactions. These characteristics can be assessed using various techniques, including temperature-programmed desorption (TPD) (Rodríguez-González *et al.*, 2007), Fourier transform infrared spectroscopy (FTIR) (Busca, 1999; Lercher *et al.*, 1996), microcalorimetry (Xie *et al.*, 2000), titration (Benesi, 1957), and nuclear magnetic resonance (NMR) (X. Yi *et al.*, 2020; Zheng *et al.*, 2011).

These techniques allow for the direct detection of hydroxyl (OH) groups in solid acids, either by FTIR or proton NMR with Magic Angle Spinning (MAS). Most methods applied at the liquid-solid or gas-solid interface utilize molecular probes, as shown in Table 1. For qualitative characterization of acidic properties, the adsorption of basic molecules such as ammonia and pyridine is widely used in ammonia TPD and FTIR techniques with pyridine and carbon monoxide (Busca, 1999; 2007).

However, highly basic probe molecules, such as ammonia and pyridine, can obscure subtle differences in the distribution of acidic sites, resulting in simplified profiles that reflect only the

presence of average acid strength. Although these techniques provide quick measurements of Brønsted and Lewis acidity in terms of quantity and strength, they have limitations in determining the distribution and precise location of acidic sites (Busca, 2007). In microporous materials, the use of probes with different steric hindrances can offer valuable insights into the location of active sites, revealing whether they are situated inside or outside the micropores (Lercher *et al.*, 1996).

Table 1 - Techniques most used for the estimation of acidity of solids.

Techniques	Common Probe Molecule	Main applications
Temperature-programmed desorption	NH ₃ , piperidine, n-butylamine, pyridine, argon.	Determination of the strength of surface acid sites and total acidity (Nascimento <i>et al.</i> , 2020).
Fourier transform infrared spectroscopy	Pyridine, piperidine, n-butylamine, amônia, trimethylphosphine, acetone, acetonitrile, Benzene, ethylene, carbon monoxide, nitrogen, 2,6-lutidina, CO.	Qualitative analysis enables the distinction between Brønsted acid sites (BA) and Lewis acid sites (LA). (Kondo <i>et al.</i> , 2010; Lercher <i>et al.</i> , 1996; Nakajima <i>et al.</i> , 2018; Parry, 1963)
Microcalorimetry	NH ₃ , CO, pyridine, piperidine	Determination of the strength and quantity of adsorbed species per unit of surface area and/or mass. (Ouqour <i>et al.</i> , 1993; Xie <i>et al.</i> , 2000).
Nuclear Magnetic Resonance	(³¹ P) - trimethylphosphine (TMP), trialkylfosfina (R ₃ PO) (¹⁵ N) - Acetonitrile, pyridine, piperidine, NH ₃ , n-butylamine. (¹³ C) – acetone (¹ H) - acetonitrile perdeuterada and pyridine.	Provides detailed acidic characteristics, including type, strength, concentration, and distribution (Kreisslet <i>et al.</i> , 2016; X. Yi <i>et al.</i> , 2020; Zheng <i>et al.</i> , 2011).

Among the available methods, solid-state NMR is the most versatile, especially when combined with theoretical calculations based on density functional theory (DFT). This approach allows for correlations to be drawn between the acidic strengths of Brønsted and Lewis sites, enabling the development of a more accurate acidity scale for solid catalysts (X. Yi *et al.*, 2020).

Different types of acidic sites can coexist on the same solid surface, necessitating detailed analysis of their distribution. Acidic and basic sites may be in close proximity on the solid surface, and their synergistic interactions add complexity to the acid-base characterization of solids (Busca, 1999, 2007).

3. Niobium Oxides

Nb(V) has a high charge and a small ionic radius (0.68 Å), making it susceptible to hydrolysis. In its oxide form, Nb(V) typically occupies octahedral sites and, to a lesser extent, tetrahedral sites (Ko *et al.*, 1990; Skrodzky *et al.*, 2019). The size of the Nb⁵⁺ ion is not suitable for fitting into the center of a regular octahedron, which results in the formation of distorted octahedral structures. These oxides are generally formed by the stacking of distorted NbO₆ octahedral units, as illustrated in Figure 1.

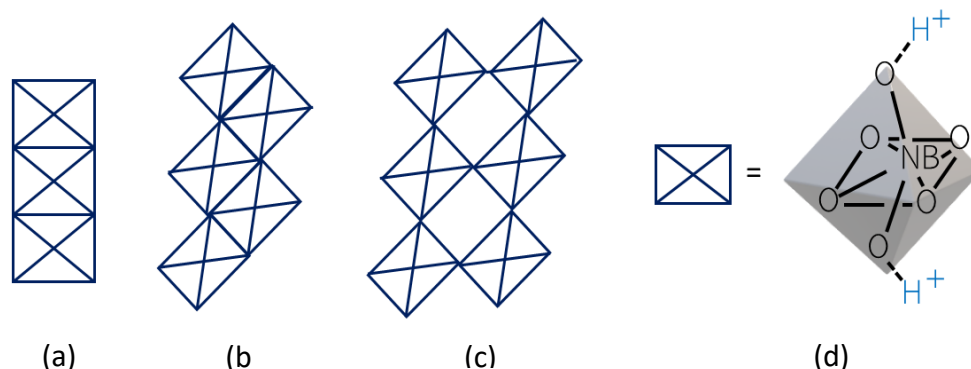


Figure 1 – Stacking configurations according to the sharing of (a) edges, (b) edges and corners, (c) corners of the NbO_6 units, and (d) representation of the distorted octahedra.

Nb_2O_5 is thermodynamically stable and readily available (Bach *et al.*, 2006), either in its amorphous form or one of its many crystalline polymorphs, which can exhibit up to 15 different structural types (Ma *et al.*, 2020; Skrodzky *et al.*, 2019). It has a crystalline structure based on interconnected NbO_6 octahedra, which share edges or corners with varying degrees of distortion (Hidde *et al.*, 2019; Nico *et al.*, 2016). The structural variability of Nb_2O_5 and niobium oxides, in general, is very similar, so the synthesis of these materials must be carefully controlled (Nico *et al.*, 2016). Control can be achieved by adjusting reaction parameters, including temperature, reaction time, and the nature of the metal precursor. Common metal precursors used to obtain niobic acid include ammonium niobium oxalate and niobium pentachloride (Heitmann *et al.*, 2019; Padula *et al.*, 2018).

The main phases of Nb_2O_5 reported in the literature include TT- Nb_2O_5 (pseudo-hexagonal), which forms at low temperatures; T- Nb_2O_5 (orthorhombic structure), obtained by heating amorphous oxide between 600 and 800°C; and H- Nb_2O_5 , with a monoclinic structure, which is the most stable phase of niobium oxide and can be formed by heating amorphous oxide to about 1100°C (Jehng *et al.*, 1991; Zhao *et al.*, 2012).

Niobic acid ($\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$) is the amorphous and hydrated form of niobium pentoxide, also referred to as niobia in the literature (Tirsoaga *et al.*, 2021). While most solid acidic metal oxides lose their acidity in the presence of water, $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ retains its catalytic activity in aqueous environments and in various liquids with different polarities and proticities (Carniti *et al.*, 2005).

When heated at low temperatures (100-300 °C), hydrated niobium pentoxide ($\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$) exhibits high acidity, comparable to 70% sulfuric acid (Tanabe, 1990). Proton NMR data suggest that the Brønsted acidity of niobic acid is very high, possibly on par with protonic zeolites (Busca 2007). A pioneering study conducted in 1983 already demonstrated the acidic and catalytic properties of $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ (Iizuka *et al.*, 1983). Since then, significant efforts have been devoted to developing new morphologies of crystalline niobium nano-oxide (or hydrated niobium oxide) with high surface areas, such as nanoparticles (Skrodzky *et al.*, 2019), rods (Ali *et al.*, 2017), layers (Dong *et al.*, 2017; Fan *et al.*, 2013), wires (Zhang *et al.*, 2020), and mesoporous materials (Liu *et al.*, 2023; Rathnayake *et al.*, 2020).

Niobium oxide structures are remarkably diverse due to the numerous bonding possibilities between octahedra and the phenomenon of crystallographic shear, which mixes different bonding regions (Zhao *et al.*, 2012). Furthermore, the presence of impurities and oxygen defects introduces variations in the typical coordination number of six, adding even more complexity to these structures (Kreissl *et al.*, 2017). These factors make studying niobium oxides challenging but also present opportunities for exploring unique properties in various applications.

As a result, many studies have focused on using niobium-based catalysts in diverse reactions, offering the potential to replace toxic acidic catalysts that can harm the production process and

generate toxic or harmful waste to humans and the environment. Table 2 provides examples of studies conducted over the past 10 years.

Table 2 – Examples of studies of acid catalysts based on Nb₂O₅.

Catalyst	-Fabrication method and >application.	Ref.
Mesoporous TT- Nb ₂ O ₅ –	- sol-gel-based inverse micelle method >Alkyne Hydration	(Rathnayake <i>et al.</i> , 2020)
Mesoporous Nb ₂ O ₅	- hydrothermal method > Fast pyrolysis of enzymatic hydrolysis lignin	(Li <i>et al.</i> , 2020)
Nb ₂ O ₅	- Thermal treatment > Glucose Dehydration to HMF in Water	(Eblagon <i>et al.</i> , 2020)
HY-340 (Nb ₂ O ₅ ·nH ₂ O) and Nb ₂ O ₅	- polymeric precursor method (Pechini method) > dihydropyrimidinones (DHPMs) fructose conversion	(Santos <i>et al.</i> , 2021)
T- Nb ₂ O ₅	- Hydrothermal treatment > Formation of Lactic Acid from a Triose Sugar in Water	(Nakajima <i>et al.</i> , 2018)
TT-Nb ₂ O ₅ , T-Nb ₂ O ₅ and pyrochlore niobium oxides	- hydrothermal method > Alkylation reaction	(Murayama <i>et al.</i> , 2014)
Nb ₂ O ₅ nanowires	- hydrothermal method > ethanolysis of furfuryl	(Zhang <i>et al.</i> , 2020)
Nb ₂ O ₅ /H ₂ SO ₄	- Chemical process with H ₂ SO ₄ > oleic acid esterification	(Sturt <i>et al.</i> , 2019)
	> Biginelli Multicomponent Reaction,	(Nascimento <i>et al.</i> , 2020)
	> hydroxyalkylation-alkylation (HAA) reaction	(Chhabra <i>et al.</i> , 2023)
Nb ₂ O ₅ /SBA-15	- mechanochemically synthesized > Friedel-Crafts alkylation reactions	(Pineda <i>et al.</i> , 2020)
Nb ₂ O ₅ /montmorillonite	- cation-exchanged synthetic method > production of HMF from glucose	(Qiu <i>et al.</i> , 2019)
Nb ₂ O ₅ /Y Zeolite	- via impregnação aquosa > glycerol conversion to produce solketal	(Ferreira <i>et al.</i> , 2018)
Nb ₂ O ₅ / mesoporous zirconium doped silica	- incipient wetness impregnation. > catalytic dehydration of glycerol to acrolein	(García-Sancho <i>et al.</i> , 2015)
Nb ₂ O ₅ -phosphorylated carbon xerogel composites	- modified deposition-precipitation method. > cascade conversion of glucose HMF in pure water.	(Eblagon <i>et al.</i> , 2023)
Nb ₂ O ₅ /carbon composites	- hydrothermal method > Conversion of cellulose into HMF	(X. Li <i>et al.</i> , 2018)
TT-Nb ₂ O ₅ or Nb ₂ O ₅ /phosphate carbon composites	- hydrothermal carbonization of cyclodextrins >Direct conversion of glucose to HMF	(Saadaoui <i>et al.</i> , 2023)
Nb ₂ O ₅ @ magnetite Nb ₂ O ₅ -SiO ₂ @ magnetite nanoparticles	- i) precipitation and ii) sol-gel method >glucose dehydration to HMF	(Tirsoaga <i>et al.</i> , 2021)

3. Niobium Pentoxide as an Acid Catalyst

Tanabe (1990) reported a significant increase in catalytic activity, selectivity, and chemical stability of traditional catalysts when small amounts of niobium were added. Until then, this metal was used almost exclusively in metallic alloys.

One of the earliest studies to investigate the nature of acid sites in niobium oxides was conducted by Ouqour *et al.* (1993). In this study, the conversion of propan-2-ol to propene (acid-catalyzed) and/or acetone (redox or acid-base catalyzed) was employed as a model reaction to characterize the acid-base properties of the catalysts. The results showed that niobium oxides can act as both Brønsted and Lewis acids, depending on the calcination temperature to which the oxide was subjected. The acidic properties of the samples were determined by NH_3 adsorption microcalorimetry at 100 °C. The total concentration of acid sites remained approximately constant up to a calcination temperature of 400 °C, decreasing sharply above that value. Furthermore, the surface area also decreased as the calcination temperature increased.

The control of material acidity through thermal treatment can be advantageous, allowing the material's properties to be adjusted to meet specific reaction needs, as demonstrated by Eblagon *et al.* (2020). In this study, the acidity of niobium pentoxide was evaluated after thermal treatment by heating the material between 300 and 550 °C, in air or an inert atmosphere (N_2). The starting material, hydrated niobium pentoxide, exhibited high surface area and high acidity (2.35 mmol/g). As the thermal treatment temperature increased up to 550 °C, $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ was gradually transformed into a pseudo-hexagonal phase. As expected, the increase in temperature led to a decrease in surface area and a reduction in the total acidity of the niobium oxide materials.

Catalytic tests showed that the catalyst obtained by calcination of niobic acid at 300 °C exhibited the highest total acidity and was highly efficient in the dehydration of fructose to HMF (5-hydroxymethylfurfural) in an environmentally friendly one-pot process. In contrast, niobic acid calcined at higher temperatures (550 °C) exhibited very low total acidity, making it more suitable for glucose isomerization to fructose, primarily due to the formation of Brønsted acid sites by rehydration in water. The influence of water on the activity of the catalysts will be discussed in the next section.

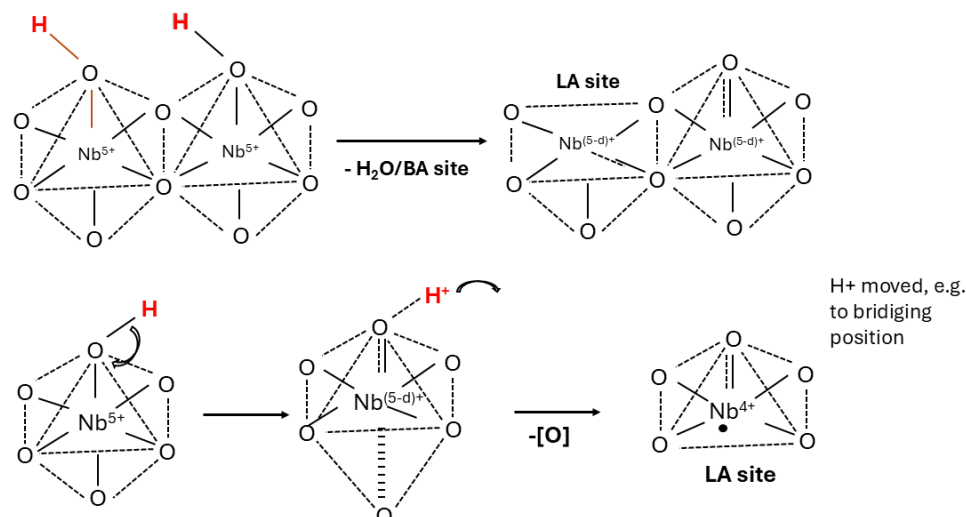
Eblagon *et al.* (2020) found that only thermal treatment of niobic acid at an intermediate temperature of 300 °C allowed for an adequate surface acidity, which resulted in acceptable glucose conversions with minimal HMF degradation into by-products. It was observed that only partial removal of surface acid sites from niobic acid enables better HMF stability in water.

The nature of the acid sites in $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ is still not completely understood. Studies suggest that both Brønsted and Lewis acid sites coexist in $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$, and these sites likely correspond to OH groups associated with NbO_6 octahedra and highly polarized tetrahedra (Lebarbier *et al.*, 2012). The complexity of the amorphous structure of $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ makes it challenging to adjust the acidity by manipulating the structure.

Thermal treatment at high temperatures, generally employed to induce structural modifications such as crystallization and phase transformations, is usually accompanied by a decrease in catalytic activity. The widely accepted theory suggests that during heating, the dehydration of two Brønsted sites results in the formation of weaker Lewis sites (Ward, 1968) (Scheme A). However, recent studies indicate that a higher number of Lewis sites can be generated after dehydration under certain synthesis conditions. The emergence of these new sites is attributed to the reduction of niobium from oxidation state V to IV (Kreissl *et al.*, 2017), as illustrated in Scheme B. This reduction appears to occur in the presence of stabilizers or templates, such as surfactants, during the synthesis of niobium oxides, leading to metal centers with lower coordination after thermal treatment.

Scheme 1 - Oxygen Vacancy/LA Site formation via (a) BA site removal in the form of water and (b) oxygen removal with Nb^{4+} formation and proton shift adapted with permission from (Kreissl *et al.*, 2017).

(a)



Studies by Siddiki and collaborators (Ali *et al.*, 2015; Ali *et al.*, 2016; Ali *et al.*, 2014; Hirunsit *et al.*, 2018) revealed that Nb₂O₅ is a highly effective heterogeneous catalyst for nucleophilic substitution reactions of carboxylic acids and their derivatives. It is particularly efficient in amidation reactions, such as the synthesis of amides from amines with carboxylic acids or esters, and the formation of cyclic imides from dicarboxylic acids or dicarboxylic anhydrides. Nb₂O₅·nH₂O also demonstrated high efficacy in the cyclization of dicarboxylic acids into cyclic anhydrides. These catalysts, which contain Lewis acid sites, have been shown to outperform group III metal triflates as Sc(OTf)₃, a well-known water-tolerant homogeneous Lewis acid catalyst, exhibiting tolerance to basic inhibitors such as water and amines. These studies led to a review (Siddiki *et al.*, 2019) focused on nucleophilic substitution reactions of carboxylic acids and their derivatives catalyzed by Nb₂O₅ and Nb₂O₅·nH₂O, addressing both experimental and computational aspects.

3.1 Nanostructured Architecture in Niobium Oxides as Acid Catalysts

The formation of nanostructured architectures, referred to as nanoarchitecture, can be tuned through techniques such as self-assembly and molecular synthesis, enabling the creation of functional materials with optimized properties (Chhabra *et al.*, 2023). A notable example is the work of García-Sancho *et al.* (2014), who prepared mesoporous Nb₂O₅ using a neutral templating method. This material was applied in the dehydration of xylose for furfural production, exploiting the presence of Lewis and Brønsted acid sites in Nb₂O₅.

The sol-gel method is widely used for the production of mesoporous materials, but it generally results in amorphous Nb₂O₅. In contrast, Rathnayake *et al.* (2020) (Rathnayake *et al.*, 2020) proposed a modified reverse micelle method to synthesize mesoporous and crystalline Nb₂O₅, specifically in the TT-Nb₂O₅ form, with adjustable pore sizes. This process utilizes the non-ionic surfactant Pluronic 123 (P123), a triblock copolymer capable of forming reverse micelles in polar protic solvents such as 1-butanol. These micelles act as nanoreactors, facilitating the migration and stabilization of Nb⁵⁺ ions within the micellar system through hydrogen bonding. After thermal treatment, the surfactant is removed, resulting in a mesoporous structure with pore sizes that can be controlled by adjusting the quantity and size of the surfactant used. The resulting material was shown to be an eco-friendly solid acid catalyst for the hydration of alkynes, demonstrating excellent catalytic activity. This high catalytic activity was attributed to the presence of Brønsted acid sites within the structure. Additionally, the catalyst could be reused for up to five cycles without significant loss of activity.

Kreissl *et al.* (2016) conducted a detailed investigation to correlate the structure of niobium oxide with its acid sites, using the conversion of sugar to HMF as a model reaction. They performed structural measurements and catalytic performance studies to elucidate the mechanism of conversion on niobium oxides. Through the ^{31}P chemical shift values obtained by NMR, they differentiated between Brønsted acid (BA) and Lewis acid (LA) sites and observed variations in the acid strength of both types of sites. In addition to NMR measurements with TMP (trimethylphosphine), the authors used the Hammett indicator method to assess the acidity of the materials. Although the absolute values obtained by these two techniques did not coincide, the trends in the number of acid sites were consistent: the total number of acid sites increased in the following order: $\text{Nb}_2\text{O}_5 < \text{HfNb}_3\text{O}_8$ (bulk) $< \text{hy-Nb-TEOA}$ (multilayers) $< \text{hy-Nb}$ (monolayers) $< \text{mesoporous amorphous Nb}_2\text{O}_5$. This trend seems closely related to the surface areas of the materials.

For hy-Nb and hy-Nb-TEOA , their structures resemble that of HfNb_3O_8 , but in the form of few-layer sheets for hy-Nb and monolayers for hy-Nb-TEOA . Interestingly, hy-Nb exhibited a larger surface area and a higher number of acid sites compared to hy-Nb-TEOA , which the authors (Kreissl *et al.*, 2016) attributed to a higher degree of layer restacking and lower porosity in the latter. The crystalline materials HfNb_3O_8 , hy-Nb , and hy-Nb-TEOA contain both strong and weak BA sites, but mesoporous amorphous Nb_2O_5 appears to contain only weak sites.

Previous studies (Takagaki *et al.*, 2010; Zheng *et al.*, 2011) indicate that strongly acidic BA sites in oxides of groups IV to VI of the periodic table are associated with the bonding of hydroxyl groups between edge- or face-sharing octahedra. In contrast, weaker BA sites correspond to protons located on terminal oxygens (Figure 2). Nuclear magnetic resonance (NMR) suggests that the degree of connectivity of NbO_6 octahedra in different forms of niobium oxides is crucial for defining the strength of these acid sites. In the case of mesoporous Nb_2O_5 , the presence of weak acid sites is attributed to its amorphous structure, where structural disorder leads to disordered vertex sharing of the octahedra, resulting in the predominance of terminal hydroxyls and, consequently, weaker BA sites.

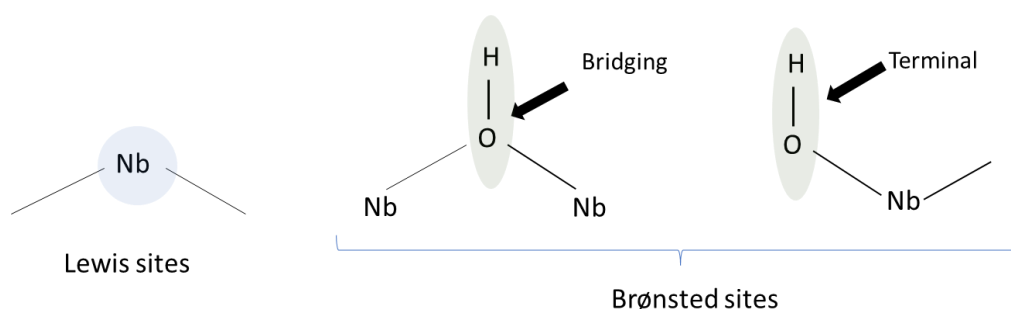


Figure 2 – Simplified representation of the possible acidic sites on niobium oxide.

The increase in the quantity and strength of Brønsted acid (BA) sites in the hy-Nb and hy-Nb-TEOA materials, compared to HfNb_3O_8 , was attributed to the reduced layer thickness and increased structural distortion, which resulted in a greater number of bridging acidic hydroxyls (Kreissl *et al.*, 2016). A subsequent study by Kreissl *et al.* (2017) demonstrated that new sites emerge due to the presence of niobium with a coordination number lower than six, generated during the synthesis process (Kreissl *et al.*, 2017).

Numerous studies have concentrated on developing niobium pentoxide (Nb_2O_5) nanomaterials to establish correlations between their structural distortions and acid catalytic performance (Kreissl *et al.*, 2017; Skrodczky *et al.*, 2019). Organic solvent-based syntheses are widely employed for producing metal oxide nanocrystals, with alcohols, amines, and carboxylic acids being the most prevalent solvents (Niederberger *et al.*, 2009; Skrodczky *et al.*, 2019). However, such methods remain underexplored for the production of solid acids.

One example is the synthesis of Nb₂O₅ nanoparticles through the reaction of NbCl₅ with acetophenone, as reported by Skrodczky *et al.* (2019). This approach yielded Nb₂O₅ nanoparticles (Nb₂O₅-NP), Nb₂O₅ nanospheres (Nb₂O₅-NS), and Nb₂O₅ nanoparticles supported on graphene oxide (Nb₂O₅-hGO). The resulting oxides exhibited orthorhombic structures with varying degrees of distortion and unsaturated niobium coordination, where the acidity was highly sensitive to these structural changes. Graphene-supported Nb₂O₅ showed a slightly distorted orthorhombic structure, predominantly featuring terminal hydroxyl groups that acted as medium to weak Brønsted acid sites. In contrast, the more significant distortions in Nb₂O₅-NP and Nb₂O₅-NS were associated with stronger Brønsted acid sites, while Lewis acid sites were attributed to highly distorted octahedral units. Although Nb₂O₅·nH₂O exhibits a similar acidity origin, the acetophenone synthesis produced Nb₂O₅-NP and Nb₂O₅-NS with higher acid site density, stronger acidity, and enhanced catalytic activity compared to conventional amorphous Nb₂O₅·nH₂O.

The morphology of niobium nanoparticles significantly impacts their efficiency as catalysts. Fuchigami *et al.* (2020) developed a catalyst with Lewis acid sites using niobium pentoxide in an intricate three-dimensional (3D) pointed nanostructure. The precise morphology of the niobium pentoxide was controlled, transitioning from a one-dimensional (1D) to a complex 3D structure through a ligand-assisted hydrothermal process, preserving its crystalline integrity. Unlike the 1D niobium pentoxide nanorods, which have distinct major and minor axes, the pointed particles maintained their nanoscaled structure even after calcination at 400°C (Fuchigami *et al.*, 2020).

These pointed particles demonstrated the highest rate of 2-(4-methoxyphenyl)amino)-2-phenylacetonitrile production in a Strecker reaction, highlighting their remarkable reactivity and structural stability. Acid site analysis and Raman spectroscopy revealed that the nanorods oriented along the (001) direction acted as Lewis acid catalysts, with the acidity attributed to a flexible Nb-O polyhedral structure in the nanoscale niobium oxide rods (<10 nm). This study suggests that pointed niobium pentoxide structures exhibit sintering resistance and high activity, offering promising applications as recyclable and regenerable solid acid catalysts (Fuchigami *et al.*, 2020).

Various factors influence the behavior of acid sites in solid materials, and the catalytic activity of Nb₂O₅ is highly sensitive to the synthesis conditions. This sensitivity is partly due to the wide variety of structures that can be obtained, which, together with structural defects, create a vast, promising, and challenging field of study that remains to be fully explored.

3. 2 The Effect of Water on Catalytic Activity

Solid acids play a fundamental role as catalysts in various industrial processes, including catalytic reactions in the presence of water, such as hydration, dehydration, and esterification. The interaction between water and the acid sites of these catalysts is crucial for developing solid catalysts that maintain high performance even in wet conditions (Dai *et al.*, 2017; Lloyd, 1994; West *et al.*, 2009).

The relationship between water and the nature of the acid sites in solid catalysts has been studied over the years. A classical example was observed by Ward (1968), who proposed that the number of Lewis acid sites increases while Brønsted acid sites decrease after thermal treatment under vacuum in Y-type zeolites. Furthermore, the hydration of Lewis acid sites can reverse this process, re-forming Brønsted acid sites (Omata *et al.*, 2020). This dynamic equilibrium between Brønsted and Lewis sites, influenced by the presence of water, is a key factor in the catalytic activity of solid acids, particularly in reactions occurring in aqueous environments. Understanding this equilibrium is essential for the design and optimization of solid catalysts for industrial applications involving water.

The shift from Lewis acid sites to Brønsted acid sites upon water adsorption in catalysts is generally observed through FTIR measurements using probe molecules such as pyridine or CO in various catalysts like alumina-silica, zeolites, and metal oxides (Kondo *et al.*, 2010; Parry, 1963; Ward, 1968). Recently, the behavior of water during actual catalytic reactions has gained attention.

Niobium oxide has been reported as a water-tolerant solid acid catalyst for various water-involved reactions (Hara, 2014; Nakajima *et al.*, 2011; Okuhara, 2002).

Dai *et al.* (2017) highlighted that most studies on the effect of water on the variation in the number and distribution of chemisorbed basic molecules (probes) on the surface of Brønsted and Lewis acid sites used only small amounts of water. This procedure was likely adopted to minimize reactor and pipeline corrosion. However, limited water usage may restrict experimental results, as the effects of water can depend on H₂O partial pressure or the H₂O-substrate ratio (West *et al.*, 2009).

To overcome this limitation, the authors used the isomerization of 3,3-dimethylbut-1-ene (33DMB) and the dehydration of 2-propanol (2PO) as model reactions to investigate the surface acidic properties of solid catalysts. Specifically, the isomerization of 33DMB occurs exclusively on Brønsted acid sites, allowing a direct evaluation of Brønsted acidity; dehydration of 2PO can occur on both Lewis and Brønsted acid sites, providing an analysis of the general surface acidity of the catalyst (Dai *et al.*, 2017).

Tests were conducted under different water amounts to generate varying partial pressures of H₂O, while the partial pressure of the reactants (33DMB or 2PO) remained constant during the reaction. For these experiments, H-ZSM-5 (Brønsted acidity), γ -Al₂O₃ (Lewis acidity), and hydrated niobium oxide (Nb₂O₅-350), known for its water-resistant surface acidity, were used as representative solid acid catalysts. The presence of water had little effect on the Brønsted acidity of H-ZSM-5 but significantly reduced the Lewis acidity of γ -Al₂O₃. In the case of Nb₂O₅-350, water caused significant poisoning of the stronger Lewis sites but also generated new, weaker Brønsted acid sites (Dai *et al.*, 2017).

A mechanism for water activation in Nb-O was proposed (Omata *et al.*, 2020), where water adsorption on the Lewis sites of Nb-O weakens the OH bond, temporarily creating Brønsted sites on the solid surface. Although the study conducted by Omata and Nambu (2020) consistently demonstrates the influence of water on the acidity of niobium oxides, the authors highlight the difficulty in determining whether water remains intact or dissociates on the Nb-O surface when acting as a Brønsted acid.

This interaction between water and solid acid catalysts is crucial for optimizing their catalytic performance in water-involved reactions, especially for processes that require stable Brønsted or Lewis acidity in humid environments. In the same study, the mechanism of benzene cracking was investigated using HZSM-5 and amorphous Nb₂O₅ catalysts. Experiments were performed on these catalysts, exchanged with sodium ions to produce Na-HZSM-5 and Na-Nb-O, both of which lack Brønsted sites. These reactions were conducted in the presence and absence of water vapor and D₂O. Despite displaying similar mechanisms, the reactions catalyzed by Na-Nb-O in the presence of water vapor showed a benzene production rate more than six times higher than those without water. Moreover, nearly all the benzene produced incorporated deuterium atoms. This suggests that deuterium was introduced into the benzene through new Brønsted sites formed by the adsorption of D₂O molecules on Nb-O (Omata *et al.*, 2020).

The findings of Vieira *et al.* (2020) further corroborate the results discussed above. They employed niobium pentoxide as a catalyst for the dehydration of sugars to 5-hydroxymethylfurfural (HMF). Previous studies had shown that Lewis acids facilitate the in situ isomerization of glucose to fructose, which is then selectively dehydrated to HMF (Gallo *et al.*, 2012; Pagán-Torres *et al.*, 2012). In the dehydration of xylose, high selectivity for furfural is typically achieved using Brønsted acids (Gürbüz *et al.*, 2013). Notably, in solvent systems containing water as a cosolvent, selectivity towards HMF increases linearly with the water content, a trend similar to that observed in benzene cracking (Omata *et al.*, 2020). This behavior suggests that Brønsted acidity in Nb₂O₅ becomes increasingly important as the water fraction in the system rises. The hydration of Nb₂O₅ leads to the formation of niobic acid, a strong acid (Nakajima *et al.*, 2011), indicating that water in the reaction mixture directly enhances Brønsted acidity (Vieira *et al.*, 2020).

However, other factors can influence the strength of the LA sites on Nb₂O₅ in nucleophilic substitution reactions of carboxylic acids. Kinetic studies with succinic acid and n-octylamine have

shown that the Nb^{5+} acid sites of Nb_2O_5 preferentially interact with carboxylic acids, even in the presence of basic molecules such as water and amines (Ali *et al.*, 2014). DFT calculations, performed with acetic acid on $\text{Nb}_2\text{O}_5(100)$ surfaces, suggest that C=O bond activation occurs through a covalent interaction between the carbonyl group and the unoccupied d orbitals of niobium, rather than a purely electrostatic interaction with acid sites (Hirunsit *et al.*, 2018). This ability of Nb_2O_5 to activate C=O bonds without competing for adsorption with basic molecules, such as amines and water, is key to its success in amidation-type reactions.

4. Optimizing Acidity in Niobium Pentoxide via Surface Modifications

An efficient and widely recognized method for modifying the surface of niobium oxides is the addition of functional groups through acid treatment (Figure 4), with sulfuric and phosphoric acids being the most common (Chhabra *et al.*, 2023; Liu *et al.*, 2023). This treatment enhances the surface acidity by introducing new acidic sites, optimizing the catalytic activity for a range of reactions. The incorporation of these groups alters the surface properties, making niobium pentoxide more versatile in catalytic applications, particularly in reactions requiring strong acidity or specific site selectivity.

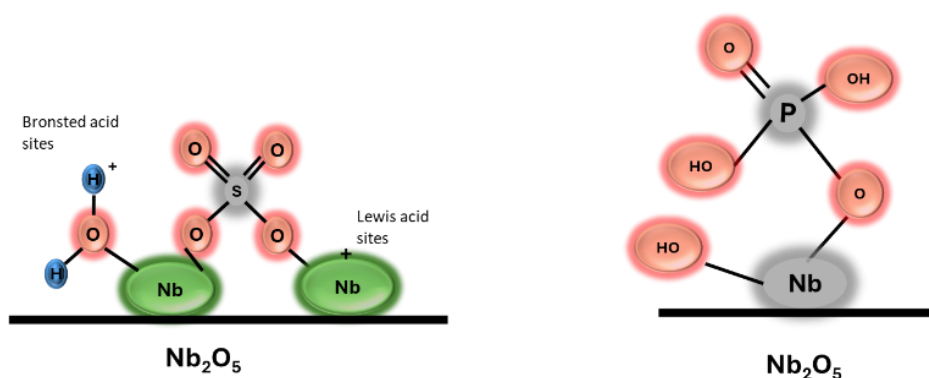


Figure 4 – Representation of functionalized niobium pentoxide: (a) $\text{Nb}_2\text{O}_5/\text{H}_2\text{SO}_4$ and (b) $\text{Nb}_2\text{O}_5/\text{H}_3\text{PO}_4$.

Studies have shown that treating $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ or Nb_2O_5 with various mineral acids results in materials with significant variations in surface area and acidity, both critical factors in catalytic processes aimed at biofuel production, such as transesterification, esterification, and pyrolysis of vegetable oils (Bassan *et al.*, 2013; Sturt *et al.*, 2019). Previous work (Brandão *et al.*, 2009; Okazaki *et al.*, 1993) already highlighted the catalytic activity of $\text{Nb}_2\text{O}_5/\text{H}_3\text{PO}_4$ in reactions of soybean oil with different alcohols. In pyrolysis processes, catalysts like Nb_2O_5 treated with H_3PO_4 , H_2SO_4 , and HNO_3 have been effective in stabilizing carboxylic acids. Additionally, in esterification reactions, $\text{Nb}_2\text{O}_5/\text{H}_3\text{PO}_4$ and $\text{Nb}_2\text{O}_5/\text{H}_2\text{SO}_4$ showed superior performance compared to pure Nb_2O_5 and $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ (Brandão *et al.*, 2009).

There are two common methods of incorporating P–OH groups into niobium oxide. The first occurs during the synthesis of niobium phosphate (NbOPO_4), when phosphoric acid is added during the process of obtaining niobium pentoxide. The second involves direct treatment of niobium pentoxide with phosphoric acid ($\text{Nb}_2\text{O}_5/\text{H}_3\text{PO}_4$), resulting in the formation of a niobium phosphate layer on the surface (Armaroli *et al.*, 2000; Okazaki *et al.*, 1993). These catalysts are particularly notable for maintaining catalytic activity in polar and protic solvents (Okazaki *et al.*, 1993). Additionally, niobium phosphates exhibit superior textural and catalytic properties compared to $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$, with the advantage of retaining these characteristics at high temperatures (Armaroli *et al.*, 2000; Catrinck *et al.*, 2017).

Surface acidity analysis through acetonitrile adsorption reveals protonic centers and medium to strong Lewis acid sites in all samples. Amorphous niobium phosphate P–OH groups exhibit stronger Brønsted acidity than Nb–OH sites (Armaroli *et al.*, 2000). Since this review focuses on niobium pentoxide, only the results obtained by acid treatment of niobium oxide were considered throughout the text.

Some reactions require control over the ratio of Brønsted and Lewis acid sites, and a promising approach is the combination of niobium oxides and phosphates (Catrinck *et al.*, 2017). Morphological and structural modifications, such as those synthesized by Chhabra and Krishnan (2023), can also increase acidity. These authors created Nb₂O₅ nanoflowers that act as Lewis acid catalysts by adding sulfonic acid groups, which increase the proportion of Brønsted acid sites. These materials were successfully applied in the reaction between 2-MF and furfural, demonstrating sustainability and ecological feasibility.

However, Nb₂O₅/HX catalysts present some limitations, such as functional group leaching under hydrothermal conditions and low dispersion of active sites. To overcome these challenges, supports like montmorillonite, carbon nanocomposites, and mixed oxides of Nb₂O₅-MeO₂ (Me = Ti, Zr, Ce) have been tested with good results (Qiu *et al.*, 2019; Saadaoui *et al.*, 2023; Stošić *et al.*, 2014).

5.0 Nb₂O₅/Supports

The dispersion of small amounts of oxides on high surface area materials generates new structural species that directly influence the catalytic activity and selectivity of these materials (Ferreira *et al.*, 2018). Early studies on niobium oxide dispersed on supports were conducted by Wachs and collaborators (Datka *et al.*, 1992; J. M. Jehng *et al.*, 1991; J.-M. Jehng *et al.*, 1990; Wachs *et al.*, 1996). These works revealed that basic surfaces favor the formation of highly distorted NbO₆ groups, while acidic surfaces promote the generation of slightly distorted NbO₆, NbO₇, and NbO₈ groups. The geometry of niobium oxide significantly affects catalytic activity: highly distorted NbO₆ groups, with Nb=O bonds, are associated with Lewis acid sites, while less distorted NbO₆, NbO₇, and NbO₈ groups contain Nb–O bonds, associated with Brønsted acid sites.

Carniti *et al.* (2008) investigated various synthesis routes for NbOx/silica materials and demonstrated that the distribution of niobium species can be controlled by adjusting the concentration of the niobium phase in the matrix, allowing modulation of the acidic and catalytic properties of the materials. One-step synthesis of Si-Nb oxides generated materials with superior characteristics compared to those obtained by simple deposition of niobia on silica (Carniti *et al.*, 2008).

Studies on Nb₂O₅ supported on silica-alumina showed that crystallite formation only occurs at calcination temperatures of 800°C or higher, a behavior attributed to Nb₂O₅-support interactions that limit niobium species mobility, preventing their aggregation into crystalline phases (Braga *et al.*, 2005). Similar behavior was observed in zeolite supports (Barros *et al.*, 2008; Ferreira *et al.*, 2018).

Micro and mesoporous supports, such as MCM-41 (García-Sancho *et al.*, 2015), SBA-15 (Pineda *et al.*, 2020), and zeolites (Barros *et al.*, 2008), have been investigated as supports for niobium oxides. The effectiveness of incorporating niobium into the structure of zeolites and mesoporous molecular sieves, as well as its influence on their catalytic activity, was extensively discussed in the review by Ziolk and Sobczak (2017).

Zeolite Y, with its faujasite-type structure, is widely used in catalysis due to its large pores and high acidity (Di Renzo *et al.*, 2005). However, the hydrophilic nature of these zeolites limits their performance in reactions involving water, such as glycerol acetalization. An effective strategy to overcome this limitation is the deposition of Nb₂O₅ on these zeolites, which imparted hydrophobicity to their surfaces. Microcalorimetric data revealed that the addition of niobium increased the percentage of irreversibly adsorbed ammonia (NaY < HY < HUSY), indicating a rise in the concentration of stronger acidic sites (Ferreira *et al.*, 2018).

Catalytic results showed that the combined acidity, hydrophobicity, and additional mesoporosity provided by Nb₂O₅ deposition were key factors in the good performance of glycerol acetalization. Among the samples studied, Nb₂O₅-HUSY demonstrated the greatest potential for applications in heterogeneous catalysis, suggesting that the combination of high acidity, hydrophobicity, and optimized mesoporosity results in superior catalytic activity (Ferreira *et al.*, 2018). An alternative niobium-based material in the literature involves the modification of niobium oxyhydroxide with cetyltrimethylammonium, producing amphiphilic catalysts that showed promising results for this reaction (Souza *et al.*, 2014; Souza *et al.*, 2015).

6. Other Advances

Huang *et al.* (2020) proposed the construction of supported catalysts through cellulose regeneration. The immobilization process of Nb₂O₅·nH₂O nanoparticles was described as follows: first, cellulose was dissolved in an aqueous NaOH/urea solution at low temperature to break the hydrogen bond networks in cellulose. Then, Nb₂O₅·nH₂O was added to the solution, followed by cellulose regeneration (Re-Cellulose). The obtained catalyst demonstrated high activity in converting glucose and fructose into HMF. FTIR results of pyridine adsorption and desorption indicated that only Lewis acid sites, and not Brønsted sites, were present in this catalyst.

The strong interactions between Nb₂O₅·nH₂O nanoparticles and the Re-Cellulose support involve extensive hydrogen bond networks, resulting in high stability and limited leaching of Nb₂O₅·nH₂O nanoparticles. The absence of Brønsted acid sites in the Nb₂O₅·nH₂O@Re-Cellulose catalyst likely contributes to the stability of HMF in water, positively affecting the yield.

Antunes *et al.* (2024) proposed a novel synthesis route for niobia-silica (Si-Nb) nanostructures using a template-free sol-gel methodology, with acetophenone as a reagent. The resulting materials consist of niobium oxide nanoparticles (~5 nm) uniformly distributed in a mesoporous silica matrix, with the Nb content ranging from 7 to 82 at.% relative to Si. The analyses revealed a specific surface area (SBET) of 224 to 913 m²/g, with mesopore sizes between 7 and 27 nm.

These materials exhibited predominantly Lewis acidity, with a lesser contribution from Brønsted acid sites. The Si-Nb catalysts showed remarkable performance in the formation of bio-based esters, yielding promising results in terms of selectivity and conversion efficiency, along with high ethanol consumption efficiency. According to the authors, these are the first fully inorganic Si-Nb catalysts reported for the conversion of α -angelica lactone/alcohol, valeric acid/alcohol, and levulinic acid/ethanol into esters, with satisfactory outcomes. This high performance is attributed to the combination of large surface area and the uniform distribution of Lewis acid sites, which facilitates the accessibility of reactants to the active catalytic sites, thereby maximizing reaction efficiency.

Moreover, the synthesis of these catalysts is fast and versatile, allowing the incorporation of different metals, which significantly broadens the scope of reactions and substrates that can be processed using these materials. These catalysts outperformed pure Nb₂O₅ as well as hydrothermally synthesized composites consisting of Nb₂O₅ nanoparticles embedded in a mesoporous silica matrix. With these characteristics, the Si-Nb materials stand out as a promising platform for biomass valorization and the sustainable production of renewable chemicals, expanding their potential applications in industrial processes, particularly within the framework of green chemistry and the circular economy.

The combination of metal oxides and phyllosilicates to form heterostructures has been widely studied in the literature (Cecilia *et al.*, 2018). Several works have focused on obtaining this combination using phyllosilicates, such as clays, and niobium species (Hass *et al.*, 2020; Marcos *et al.*, 2016; Qiu *et al.*, 2019). A recent study by Oliveira *et al.* (2024) described the synthesis of clay pillared with niobium oxides.

In this study, niobium pentaethoxide, Nb(OEt)₅, was used as a niobium source. The natural clay was pre-treated with cetyltrimethylammonium, a quaternary amine, which increased the interlayer spacing of montmorillonite from approximately 13 to 20 Å. The authors suggested that

under the synthesis conditions, the niobium precursor hydrolyzed upon contact with the organophilic medium in the interlamellar region. After calcination at 400°C, the organic matter was removed, and niobium species were converted to niobium oxide, maintaining the clay sheets separated and allowing greater access of molecules to internal surfaces (Oliveira *et al.*, 2024).

The pillared materials exhibited acidic characteristics, with strong Brønsted and Lewis sites. The results indicate a synergistic interaction between these sites, where the strength of Brønsted sites is enhanced by the presence of Lewis sites. The niobium oxide pillars are covalently bonded to the tetrahedral sheets of the clay. Acidic properties were further enhanced by incorporating phosphotungstic acid ($\text{H}_3\text{PW}_{12}\text{O}_{40}$ – HPW), which was added during the intercalation step. This study stood out for the height of the niobium oxide pillars, which was greater than that reported in previous works (Gallo *et al.*, 2006; Qiu *et al.*, 2019). The choice of niobium source and organophilization step were likely key to the success of clay pillaring.

The results demonstrated that the heteropoly acid is located in the inter-pillar spaces of the pillared clays. The conversions obtained in esterification reactions showed that the prepared material possesses promising acidic properties, with potential applications in processes requiring strong acids, such as petroleum cracking and biomass transformation.

7. Conclusion

The acid sites in niobium pentoxide are highly sensitive to structural changes, which are, in turn, influenced by synthesis processes. This presents a significant challenge, but also opens up a vast field of exploration for the creation of new materials. While much is known about the impact of temperature on these sites, there remains much to be discovered regarding the role of solvents and copolymers. The material's morphology and porosity significantly affect octahedral distortions, which can enhance surface acidity. Therefore, nanometer-scale materials appear to be a promising area for future investigation.

Moreover, the ability of niobium pentoxide to function as an acid catalyst can be further improved by incorporating other functional groups, such as those containing sulfur and phosphorus, as well as organic molecules. These materials can also be supported on carriers, and new versatile routes are emerging, allowing the immobilization of these catalysts at the nanoscale onto novel materials, further expanding their application potential. The capacity of their active sites to remain effective in the presence of diverse environments broadens the scope for use. The combination of controlled synthesis, functionalization, and support utilization offers a vast field for the development of more efficient and selective catalysts.

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