

Evaluating the Potential of Modified Niobium (V) Oxide as Catalyst for 5-Hydroxymethylfurfural (HMF) Production : A Literature Review

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Abstract

Selectively producing 5-hydroxymethylfurfural (HMF) from biomass-derived carbohydrates is key in valorizing renewable resources into biobased chemicals and fuels. HMF is a crucial bio-based platform chemical, but its selective production from glucose and fructose remains challenging due to side reactions and product degradation. Modified niobium(V) oxide (Nb₂O₅) catalysts have shown great promise owing to their intrinsic Brønsted and Lewis acidity, thermal stability, and surface tunability. This review overviews recent advances in catalyst design, including metal doping, structural tuning, and hybridization with porous materials. These have significantly improved HMF yields -up to 80%- while enhancing catalyst selectivity and reusability. A systematic review with a descriptive-analytical approach was applied, analyzing literature from 2015 to 2025 across major scientific databases. Furthermore, challenges, including side-product formation and active site leaching, are highlighted alongside future perspectives for scalable and green HMF synthesis using Nb-based catalysts. This review aims to guide the rational development of modified Nb₂O₅ catalysts for efficient biomass transformation. These developments are crucial for advancing Nb-based catalytic platforms and unlocking the full potential of HMF in a circular, bio-based chemical industry.

Keywords: Niobium(V)Oxide, Catalyst Modification, Fructose Conversion, Glucose Conversion, Brønsted-Lewis Acid, HMF, 5-Hydroxymethylfurfural.

1. INTRODUCTION

Environmentally friendly and sustainable chemical processes have driven extensive exploration into the utilization of renewable biomass-based feedstocks as an alternative. The synthesis of sugars derived from waste lignocellulosic biomass into valuable chemical substances has recently received significant interest as part of developing sustainable and renewable bioprocesses. For the industrial sector, recycling waste has advantages from both an environmental and economic point of view (Cazier et al., 2024). Among various bio-based platform chemicals, 5-hydroxymethylfurfural (HMF) has emerged as a key intermediate due to its versatility in producing high-value chemicals and fuels such as 2,5-furan dicarboxylic acid (FDCA), 2,5-dimethyl furan (DMF) and levulinic acid derivatives (El Fergani et al., 2021).

HMF is commonly synthesized through the acid-catalyzed dehydration of sugars such as fructose and glucose; it serves as a crucial bridge between renewable carbohydrates and functional materials for the chemical industry. The yield and selectivity of the 5-HMF product are determined by the specific surface area, structure, particle size, type of acid catalyst, and acid strength (Xu et al., 2022). The significant

challenges of production HMF remain in achieving high selectivity and efficiency in the production process. During the dehydration process, there is a tendency for the product to undergo degradation into humin and other unwanted by-products. This degradation will reduce the overall HMF yield and also diminish the selectivity of the conversion process (El Fergani et al., 2021). An acid-based catalyst with tailored surface properties was used to address this degradation issue. These catalysts are particularly appealing due to their high surface area, which can enhance catalytic activity and stability (Zhu et al., 2022). Therefore, the development of heterogeneous acid catalysts possessing both Brønsted and Lewis acid sites is essential to enhance catalytic performance in biomass conversion processes.

Niobium(V) oxide (Nb_2O_5) has attracted considerable interest as a solid acid heterogeneous catalyst due to thermal stability, amphoteric acid properties, and surface redox activity (Oliveira et al., 2023). The presence of both Lewis and Brønsted acid sites on Nb_2O_5 allows it to catalyze carbohydrate dehydration reactions effectively. Consequently, many strategies have been explored to modify niobium-based catalysts, including metal doping, structural tuning (e.g., increasing surface area), and compositing with supports such as mesoporous silica or carbon-based material. Several studies have validated these approaches. El Fergani et al. (2021) reported that graphite-supported Nb-based bifunctional catalyst achieved up to 90% HMF yield from fructose (El Fergani et al., 2021). Similarly, Chhabra & Krishnan (2023) demonstrated that a sulfonic acid-functionalized Nb_2O_5 was effective in hydroxy alkylation-alkylation (HAA) reaction, achieving a maximum yield of 87% of C-15 biofuel intermediates (Chhabra & Krishnan, 2023). In another recent study, Lima et al. (2024) utilized Nb_2O_5 to valorize carbohydrates in the microalga *Chlorella sp.* to produce added products such as 5-HMF and furfural by optimizing reaction conditions. The result indicated that the most effective Nb_2O_5 catalyst for valorizing *Chlorella sp.* into furans exhibited a greater number of Brønsted acid sites, achieving conversion yields of approximately 20-22% for 5-HMF and furfural (Lima et al., 2024). These modifications aim to tailor the acid site distribution, enhance surface accessibility, and improve catalytic efficiency.

Despite the various advancements achieved in catalytic systems of niobium (V) oxide, significant gaps remain unaddressed. These include an incomplete understanding of the synergistic role between Brønsted and Lewis acid sites of niobium(V) oxide catalyst, as well as considerable challenges in scaling up production that utilizes environmentally green solvents and operates under mild reaction conditions. Moreover, few studies provide comparative assessments of different Nb_2O_5 modifications across varied carbohydrate sources, limiting broader applicability. This review aims to provide an overview of (i) the fundamental properties of niobium(V) oxide catalysts, (ii) modification strategies of niobium-based catalysts, and (iii) recent advances and ongoing challenges in the conversion of both simple and complex carbohydrates into 5-hydroxymethylfurfural (HMF). This study also highlights future directions in catalyst design and process integration to support the development of efficient and sustainable catalytic systems. Through this analysis, the review provides new insights into the structure and activity relationships of Nb-based catalysts, supporting their advancement for industrial applications in biomass valorization.

2. METHOD

This review was conducted through a systematic review with a descriptive-analytical approach of the most recent and relevant scientific literature related to the modification and catalytic performance of niobium(V) oxide in the production of 5-

hydroxymethylfurfural (HMF). The review is structured to synthesize and critically evaluate research findings from a broad range of peer-reviewed scientific sources. First, the literature selection process was initiated through a search of academic databases, including Scopus, ScienceDirect, MDPI, ResearchGate, Google Scholar, ACS Publications, and Nature, focusing on publications from the last ten years. The search employed combinations of keywords such as “*niobium oxide*,” “*Nb₂O₅*,” “*modified catalyst*,” “*functionalized niobium*,” “*5-hydroxymethylfurfural*,” “*5-HMF*,” “*biomass conversion*,” “*glucose dehydration*,” “*fructose dehydration*,” “*acid catalyst*,” and “*Brønsted-Lewis acidity*.” Subsequently, articles were selected based on predefined inclusion criteria, which required the use of Nb₂O₅ or modified Nb₂O₅ as a catalyst for HMF production, the availability of quantitative data on catalytic performance, and detailed information on catalyst characterization, including surface area, acidity, and structural properties.

Conversely, studies relying solely on homogeneous or enzymatic systems without any niobium component were excluded to maintain a clear focus on heterogeneous niobium-based catalysis. Following the identification and screening of relevant studies, key data were extracted, including catalyst composition, feedstock type (e.g., fructose, glucose), solvent systems, reaction conditions (temperature and time), and HMF yield and selectivity. The collected data were then analyzed through a comparative, thematic synthesis, focusing on the relationship between catalyst modification strategies, acidic properties (Brønsted and Lewis acidity), and reaction outcomes. Emphasis was placed on understanding how surface functionalization, doping, and hybridization affect catalytic efficiency and selectivity in HMF production. A summary of the methodologic approach employed in this review is presented in Table 1.

Table 1. Methodological Approach Used in This Review

| Step | Description |
|----------------------|---|
| Literature Databases | Scopus, ScienceDirect, MDPI, ResearchGate, Google Scholar, ACS Publications, and Nature |
| Time Period | Publications from 2015 to 2025 |
| Search Keywords | “Niobium oxide,” “Nb ₂ O ₅ ,” modified catalyst,” “functionalized niobium,” 5-hydroxymethylfurfural”, “5-HMF”, “biomass conversion,” glucose dehydration,” fructose dehydration,” “acid catalyst,” “Brønsted-Lewis acidity” |
| Inclusion Criteria | Use of Nb ₂ O ₅ or modified forms as the catalyst for HMF production, quantitative catalytic data reported, and in-depth catalyst characterization included |
| Exclusion Criteria | Homogeneous/enzymatic systems without Nb |
| Data Extraction | Catalyst composition, Feedstock used (glucose, fructose, etc.), solvent system, reaction temperature & time, HMF yield and selectivity |
| Analysis Method | Comparative discussion based on catalyst modification strategies, acid properties, reaction efficiency |

3. RESULTS AND DISCUSSION

3.1 5-Hydroxymethylfurfural (HMF) : Sources, Synthesis, and Applications

5-Hydroxymethylfurfural (HMF) has a hydroxymethyl and an aldehyde functional group (Wang et al., 2024). HMF is a key molecule that can be derived from lignocellulosic biomass via acid-catalyzed dehydration of hexoses, such as glucose and fructose (Vieira et al., 2020;Bi et al., 2025). The most common feedstocks for HMF production include monosaccharides like fructose, which exhibits higher dehydration reactivity, and glucose, which is more abundant but requires isomerization prior to dehydration (Kreissl et al., 2016). More complex carbohydrates such as cellulose, starch,

and inulin can also serve as precursors after hydrolysis to monomeric sugars (Wang et al., 2024).

The predominance of Lewis acid sites facilitated the isomerization of glucose to fructose, which is consistent with the mechanistic insights reported by Agarwal et al. (2018), wherein glucose is converted via a Lewis acid-catalyzed step prior to acid-catalyzed dehydration (Agarwal et al., 2018). This observation aligns with Kreissl et al. (2017), who identified the niobium oxides exhibiting stronger Lewis acid character and weaker Brønsted acidity achieve superior catalytic activity for HMF production, particularly from fructose substrates (Kreissl et al., 2017).

Comparatively, the catalytic efficacy achieved herein is on par with the work by Lima et al. (2024), who successfully employed Nb₂O₅ catalysts for the HMF synthesis from *Chlorella sp.* microalgae biomass. The research of Lima et al. (2024) confirms the versatility of Nb₂O₅ as a heterogeneous catalyst across diverse carbohydrate feedstocks, ranging from simple monosaccharides to complex lignocellulosic materials, as also documented by Wang et al. (2024). Our findings corroborate the assertion by Adam Omer Ishag et al. (2019) and Catrinck et al. (2020) regarding the potential of non-food biomass wastes, such as rice straw, sugarcane bagasse, and corncob, as sustainable substrates for HMF production. Figure 1 illustrates the schematic pathway for the conversion of hexoses to HMF. Table 2 provides a summary of HMF production from different carbohydrate substrates using Nb₂O₅-based catalysts.

A notable challenge encountered, as reported in the literature Wang et al., (2024), involves the instability of HMF in aqueous acidic environments, where rehydration leads to levulinic acid and formic acid formation, alongside humin byproducts that reduce overall HMF yield. Consistent with previous studies, the implementation of biphasic reaction systems (e.g., water-organic solvent mixtures), ionic liquids, and deep eutectic solvents emerges as a promising approach to stabilize HMF and suppress side reactions, thereby enhancing product selectivity. Due to its bifunctional structure, HMF is considered a central intermediate in green chemistry and biorefinery schemes. Major downstream applications such as (i) 2,5-furandicarboxylic acid (FDCA), a monomer for bio-based polyethylene furanoate (PEF), a renewable alternative to PET, (ii) 2,5-dimethylfuran (DMF), a high-energy-density liquid biofuel with superior combustion properties to ethanol, and (iii) Levulinic esters and amino alcohols, intermediates in the synthesis of pharmaceuticals, plasticizers, and surfactants (Liu et al., 2017; Tirsoaga et al., 2020). The results presented in this study are expected to provide valuable insights into the design of acid catalysts for the sustainable valorization of both simple and complex carbohydrates into more valuable chemical compounds, supporting the advancement of green chemistry.

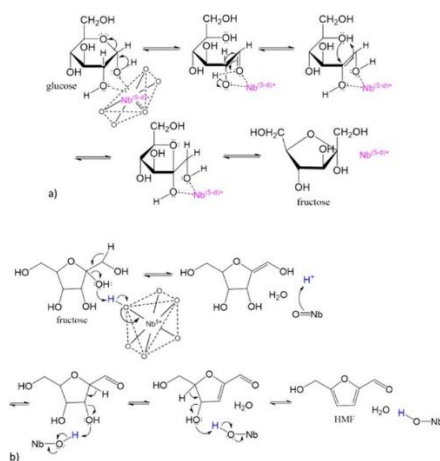


Figure 1. The schematic pathway for sugar conversion (a) glucose isomerization to fructose catalyzed by exposed Nb centers/Lewis Acid sites; (b) fructose conversion to HMF catalyzed by weaker Bronsted Acid sites/terminal hydroxyls (Kreissl et al., 2017)

Table 2. Summary of HMF Production from Different Carbohydrate Substrates Using Nb₂O₅-Based Catalysts

| Substrate | Reaction System | HMF Yield (%) | Catalyst Type | Reference |
|------------|--|---------------|--|------------------------|
| Fructose | DMSO; 120°C; 90 min | 74 | Nb-W oxide | (Ren et al., 2023) |
| Glucose | Water; 180°C; 30 min | 31 | Niobium oxide-phosphorylated carbon xerogel composites | (Eblagon et al., 2023) |
| Sucrose | DMSO; 140°C; 2 h | 65.4 | Niobium-modified montmorillonite | (Zhu et al., 2022) |
| Cellobiose | Biphasic solvents (methyl isobutyl ketone/saturated salt water; 170°C; 3 h | 68.6 | Niobium-modified montmorillonite | (Zhu et al., 2022) |

3.2 Niobium (V) Oxide (Nb₂O₅) as Catalyst

Niobium oxide is a chemical compound contained in niobium (Nb) and oxygen. It is a valuable substance due to its unique properties and numerous applications in catalysis, electronics, and energy storage industries. Niobium oxides have three unique structural phases: NbO, NbO₂, and Nb₂O₅, making Nb-O systems extremely hard to investigate. Nb₂O₅ (Niobium(V) oxide) and its closely related nonstoichiometric forms represent the largest group of niobium oxides (Kreissl et al., 2017). Typically, for solid acid metal oxides, Brønsted acid sites are protonic surface sites characterized by strongly acidic bridging or terminal hydroxyl groups. Lewis acid sites originate from electron-deficient metal centers, resulting from decreased coordination numbers or distortion of coordinating oxygen. Niobium(V) oxide and niobic acid can be amorphous. However, they begin to crystallite at approximately 500°C. Thermal treatment techniques exceeding 500°C diminish the acidic characteristics of these compounds. Kreissl et al. (2017) proposed a mechanism for the formation of oxygen vacancies or Lewis acid sites via oxygen removal accompanied by Nb⁴⁺ formation and proton shift, as illustrated in Figure 2.

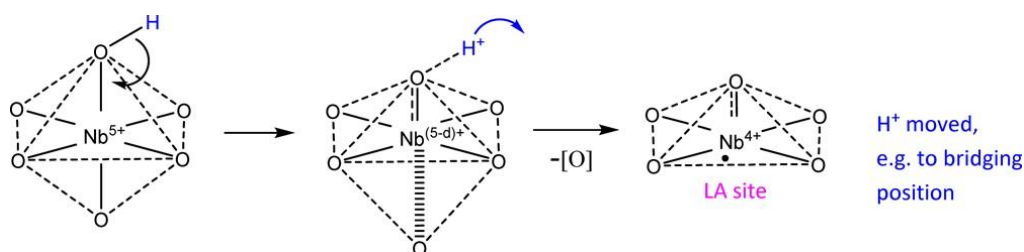


Figure 2. Scheme of proposed oxygen vacancy/Lewis Acid site formation via oxygen removal accompanied by Nb⁴⁺ formation and proton shift (Kreissl et al., 2017).

Niobium (V) oxide (Nb₂O₅) has attracted increasing attention as a solid acid catalyst in biomass valorization due to its unique acid-base properties and thermal stability. Its classification as a group V transition metal oxide endows Nb₂O₅ with a dual acidic nature, containing both Brønsted and Lewis acid sites, which are crucial for facilitating acid-catalyzed reactions such as carbohydrate dehydration to 5-hydroxymethylfurfural (HMF). Niobic acid exhibits strong acidity and functions as a water-tolerant catalyst, possessing

two distinct types of active. Structurally, the surface of Nb₂O₅ is characterized by a distorted polyhedral framework where surface hydroxyl (-OH) groups serve as Brønsted acid (BA) sites. At the same time, NbO₄ tetrahedra constitute Lewis acid (LA) sites (Eblagon et al., 2020). The material exhibits a high dielectric constant and a range of oxidation states, which contributes to its catalytic versatility. Its surface is characterized by coordinatively unsaturated niobium centers (Lewis acid sites) and hydroxyl groups capable of proton donation (Brønsted acid sites) (Kreissl et al., 2016). This bifunctional acidity is fundamental to its catalytic versatility, enabling it to efficiently mediate both isomerization, a critical preliminary transformation in HMF synthesis (Son Le et al., 2022).

When benchmarked against traditional mineral acids (e.g., HCl, H₂SO₄) and zeolite catalysts, Nb₂O₅ presents notable advantages. It is environmentally benign as a non-corrosive solid acid catalyst, circumventing issues related to acid neutralization and equipment degradation; it exhibited remarkable stability and reusability over multiple reaction cycles under mild to moderate conditions, which is essential for sustainable process design; and its acid site density and surface chemistry can be precisely tuned through synthesis and post-synthetic modifications to optimize catalytic performance for various biomass-derived feedstocks. These characteristics have been well-documented in previous studies, confirming that Nb₂O₅ is a highly promising catalyst for the production of HMF. The variable oxidation states contribute to enabling interaction with diverse substrates and reaction intermediates (Kreissl et al., 2016; Eblagon et al., 2020). Overall, the integration of strong, tunable acid sites with structural stability positions Nb₂O₅ as an advanced solid acid catalyst, facilitating the sustainable production of platform chemicals such as HMF from renewable biomass resources.

3.3 Modification Strategies of Niobium(V) Oxide

Numerous modification strategies have been extensively investigated to modulate the surface attributes and catalytic behavior of Nb₂O₅ in the context of HMF production. Table 3 summarizes key studies focusing on modified Nb₂O₅ catalysts, highlighting approaches such as metal doping, structural engineering, and composite formation with porous supports. Metal cations into the Nb₂O₅ lattice have emerged as a reliable strategy to modify the electronic properties, acid site distribution, and redox characteristics of the catalyst. Transition metal dopants, including Al³⁺, Zr⁴⁺, or Ti⁴⁺, have been reported to enhance Lewis acidity while concurrently suppressing side reactions that detract from HMF selectivity (Ji et al., 2019). These modifications fundamentally alter the surface chemistry, enabling improved catalytic specificity.

Structural engineering techniques focusing on pore architecture and surface area significantly influence catalytic accessibility and mass transfer. The application of templating agents, soft templates such as surfactants, or hard templates like carbon spheres, during synthesis, can produce mesoporous Nb₂O₅ materials with surface areas exceeding 100 m²/g, thereby facilitating improved interaction with bulky biomass-derived substrates. For instance, Tirsoaga et al. (2021) synthesized Nb₂O₅@SiO₂@MNP nanocomposites using CTAB surfactant, which exhibited high catalytic activity in indirect glucose dehydration to HMF. Similarly, the fabrication of Nb₂O₅ nanostructures such as nanowires, nanotubes, or nanosheets enhances active site exposure and mitigates diffusion limitations, correlating with increased catalytic efficiency as observed in Tirsoaga et al. (2021).

Thermal treatment parameters critically affect catalyst performance. Excessive calcination temperatures have been shown to induce crystallization and surface area loss, which detrimentally impacts acidity and catalytic activity. Ren et al. (2023) demonstrated

that higher calcination temperatures decreased the acid site density of Nb-W oxide catalysts from 0.44 to 0.21 nm⁻², resulting in reduced HMF selectivity during fructose dehydration. The study by Ren et al. (2023) demonstrated that increasing the calcination temperature of niobium-based catalysts results in a decline in HMF selectivity, which indicates a reduction in the catalyst's acidity, primarily attributed to decreased BET surface area and pore volume. Therefore, it is crucial to emphasize the implementation of optimized thermal protocols to maintain the delicate balance of surface properties.

Moreover, dispersing Nb₂O₅ onto high-surface-area supports such as silica, alumina, carbon, zeolites, or metal-organic frameworks (MOFs) represents a reliable technique to enhance catalyst stability and control acid site distribution. Mesoporous Nb₂O₅-Beta zeolite composites, for example, integrate residual framework aluminum acid sites with extra-framework isolated Nb(V) species, producing moderate-strength Brønsted acidity attributable to Nb(V)O-H groups (Candu et al., 2019).

Surface functionalization further refines catalytic properties by tuning acid strength and distribution. Grafting of sulfonic or phosphonic acid groups onto Nb₂O₅ has been demonstrated to enhance Brønsted acidity. In contrast, defect engineering- via the introduction of oxygen vacancies or hydroxyl defects- modulates electron density, amplifying Lewis acidity. In this vein, Eblagon et al. (2023) reported a bifunctional catalyst wherein Nb₂O₅ was anchored onto phosphorylated carbon xerogel surfaces, incorporating oxygen- and phosphorus-containing groups that contributed to improved Brønsted acidity and higher selectivity toward HMF. Taken together, these modifications aim to fine-tune the interplay between Brønsted and Lewis acid sites, which is imperative for the tandem isomerization-dehydration mechanism underlying efficient glucose conversion to HMF. Table 4 provides the critical impact of these catalyst design strategies on elevating catalyst performance in terms of activity, selectivity, and stability, consequently advancing Nb₂O₅-based catalytic systems for sustainable biomass valorization.

Table 3. Categories of Nb₂O₅ Modifications and Catalytic Performance for HMF Production

| Modification Strategy | Approach/ Material | Effect on Catalytic Performance | Representative References |
|---------------------------|---|---|--|
| Metal Doping | Al, Ti, Zr, Sn | Tuned acidity; improved glucose conversion; suppressed side reactions | (Ji et al., 2019) |
| Support immobilization | Mesoporous silica (SBA-15, MCM-41), ZrO ₂ | Increased surface area; improved dispersion of Nb species | (Guo et al., 2017); (Costa et al., 2023); |
| Composite/Heterostructure | Nb ₂ O ₅ -Carbon, Nb-TiO ₂ , Nb ₂ O ₅ /Zeolite | Enhanced stability and mass transfer; synergistic acid-base sites | (Tirsoaga et al., 2021); (Khumho et al., 2021); (Candu et al., 2019) |
| Surface functionalization | Sulfation, Phosphate grafting | Stronger Brønsted acidity, promoted dehydration activity | (Saadaoui et al., 2023) |

Table 4. Selected Studies on Nb₂O₅ and Modified Nb₂O₅ Catalysts for HMF Production

| Author (Year) | Catalyst Composition | Feedstock | Solvent System | Temp (°C) | HMF Yield (%) | Notes |
|---------------------|--------------------------|-----------|------------------------------|-----------|---------------------------------|-------------------------------------|
| Zhang et al. (2015) | Porous niobium phosphate | Glucose | Water; biphasic water/methyl | 140 | 33.3 (water); 39.3 (water/mehy) | The catalyst demonstrated excellent |

| Author (Year) | Catalyst Composition | Feedstock | Solvent System | Temp (°C) | HMF Yield (%) | Notes |
|------------------------|---|-----------|-----------------|-----------|---|---|
| | | | isobutyl ketone | | 1 isobutyl ketone | performance in the selective conversion of glucose in a biphasic medium |
| do Prado et al. (2016) | Nanostructured niobium oxide | Fructose | Aqueous; DMSO | 130 | 22 (aqueous medium); 47 (DMSO) | Nanostructured niobium oxide, synthesized in the form of rods or spheres, exhibits a larger BET surface area |
| Kreissl et al. (2016) | Nb ₂ O ₅ ; HNb ₃ O ₈ ; hy-Nb-TEOA, hy-Nb, Meso Nb ₂ O ₅ | Sucrose | Water | 180 | 17 (Nb ₂ O ₅); 25 (HNb ₃ O ₈); 27 (hy-Nb-TEOA), 32 (hy-Nb); 36 (Meso Nb ₂ O ₅) | Mesoporous niobium oxide demonstrated the highest HMF yield in the catalytic conversion of sucrose |
| Candu et al. (2019) | Nb-BEA | Glucose | Water | 180 | 84.5 | The catalyst exhibits moderate Brønsted acidity, which contributes to its selective catalytic performance |
| Eblagon et al. (2020) | Nb ₂ O ₅ | Glucose | Water | 180 | 37 | Amorphous Nb ₂ O ₅ exhibited a high surface area (366 m ² /g) and substantial acidity (2.35 mmol/g), contributing to its enhanced catalytic performance |
| Tirsoaga et al. (2021) | Nb ₂ O ₅ @MNP; Nb ₂ O ₅ @SiO ₂ @MNP | Glucose | Distilled water | 180 | 32.9 at (3x) Nb ₂ O ₅ @SiO ₂ @MNP; 11.73 after 8 h | Highly efficient catalyst for the dehydration of glucose to HMF |
| Eblagon et al. (2023) | Niobium oxide-phosphorylated carbon xerogel composites | Glucose | Water | 180 | 31 (30 min) | A bifunctional catalyst was prepared via deposition-precipitation of Nb ₂ O ₅ onto the surface of phosphorylated carbon xerogel (CX_P), incorporating Brønsted acid sites derived from oxygen and phosphorus, |

| Author (Year) | Catalyst Composition | Feedstock | Solvent System | Temp (°C) | HMF Yield (%) | Notes |
|------------------------|---|---------------------------------|-----------------------------------|-----------|---------------|--|
| | | | | | | containing functional groups |
| Saadaoui et al. (2023) | Niobium oxide/phosphate-carbon composites | Glucose | NaCl-water/methyl isobutyl ketone | 150 | 32-34 | Nb-based composites with high meal loadings (~20%) were synthesized via hydrothermal carbonization, followed by calcination and subsequent H ₃ PO ₄ adsorption |
| Lima et al. (2024) | Nb ₂ O ₅ | Microalgae <i>Chlorella sp.</i> | Water | 180 | 22 | Catalyst exhibiting the highest density of Brønsted acid sites were found to be the most effective for the conversion of complex biomass, such as <i>Chlorella sp.</i> , into HMF |

3.4 Catalytic Performance of Modified Nb₂O₅ in HMF Production

The modification of niobium(V) oxide (Nb₂O₅) has markedly improved its catalytic efficiency for converting glucose and fructose into 5-hydroxymethylfurfural (HMF). Consistent with established kinetics, fructose dehydration generally achieves higher HMF yields owing to its more favorable reaction pathway and reduced activation barriers. Modified Nb₂O₅ catalysts, particularly those supported on mesoporous silica or doped with Lewis acidic species, have demonstrated substantial improvements in fructose-to-HMF conversion efficiency. Zhu et al. (2022) reported the use of niobium-modified montmorillonite, wherein the active [NbO(OH)₂]⁺ species effectively lowered the activation energy of glucose isomerization by facilitating synergistic proton transfer mechanisms, thereby enhancing overall catalytic activity during cellobiose and sucrose conversion.

Conversely, glucose conversion remains more challenging due to the prerequisite isomerization step to fructose prior to dehydration. Dual-acid Nb₂O₅-based catalysts that simultaneously provide Lewis and Brønsted acid sites have shown promising efficacy in overcoming this limitation. According to Ji et al. (2019) niobium-doped TiO₂ catalysts can improve the energy efficiency of HMF production by approximately 49%, emphasizing the significance of balanced acid site distribution and catalyst design. The employment of mesoporous supports further contributes to improved mass transport and enhanced accessibility of catalytic sites, which in turn suppresses humin formation and minimizes side reactions. Supporting this, Guo et al. (2017) synthesized mesoporous Nb-W oxide characterized by a high density of Lewis and Brønsted acid sites, which promoted glucose isomerization followed by fructose dehydration, achieving notable catalytic stability in aqueous medium.

Catalyst longevity and reusability are crucial for sustainable biomass conversion processes. Modified Nb₂O₅ catalysts typically exhibit excellent thermal and hydrothermal stability, especially when immobilized on inert frameworks such as SiO₂ or incorporated

into hybrid composite materials. Tirsoaga et al. (2021) successfully synthesized $\text{Nb}_2\text{O}_5@\text{SiO}_2@\text{MNP}$ catalysts via a sol-gel approach combined with CTAB-assisted precipitation, achieving a catalytic system optimized for selective glucose dehydration to HMF. Characterization techniques, including X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), and ammonia temperature-programmed (NH₃-TPD), confirmed that these catalysts retained their structural integrity and acid site distribution after multiple catalytic cycles, reinforcing their suitability for practical applications.

3.5 Challenges and Future Perspectives

Despite significant advancements in the development of modified niobium(V) oxide (Nb_2O_5) catalysts for the efficient production of 5-hydroxymethylfurfural (HMF), several scientific and technical challenges persist that limit the translation of these systems to industrial-scale biomass valorization. Effectively managing these concerns is necessary to fully exploit the advantages of Nb-based catalytic platforms for sustainable biorefineries. A principal limitation in the acid-catalyzed dehydration of glucose and fructose is the formation of undesired by-products such as levulinic acid, formic acid, and insoluble humins. These side reactions are often attributed to excessive Brønsted acidity and prolonged residence times in aqueous media, which promote secondary degradation pathways (El Fergani et al., 2021). Although the dual Brønsted-Lewis acid character of Nb_2O_5 enables the sequential isomerization of glucose to fructose and subsequent dehydration, achieving an optimal balance between these acid sites remains a formidable challenge. Fine-tuning this balance is essential to steer reaction pathways away from retro-aldol cleavage and condensation reactions that reduce HMF selectivity.

While Nb_2O_5 -based catalysts generally exhibit commendable thermal and hydrothermal stability, long-term exposure to aqueous or acidic environments can provoke structural deterioration, pore blockage, and leaching of active niobium species, thereby impairing catalytic longevity. In addition, despite extensive surface characterization, the precise identity and distribution of active sites mediating the discrete steps in glucose-to-HMF conversion are not yet fully elucidated. A comprehensive molecular-level mechanistic understanding is imperative for the rational design of catalysts with improved selectivity and activity. To this end, leveraging advanced spectroscopic techniques (e.g., FTIR, Raman, XAS) integrated with density functional theory (DFT) simulations is crucial to unravel the structure-activity relationships of Nb-based catalysts under realistic reaction conditions.

Looking forward, several strategic directions should be prioritized to overcome these barriers and propel the field toward industrial relevance:

1. The design of multifunctional Nb_2O_5 -based catalysts incorporating atomically dispersed dopants or single-atom active sites to modulate acid-base properties and enhance catalytic performance precisely;
2. The integration of Nb catalysts into continuous flow reactor systems to improve productivity, reduce reaction times, and minimize the formation of side products through superior process control;
3. The development of green solvent systems that are compatible with Nb_2O_5 catalysts and facilitate selective HMF extraction to enhance yield and catalyst stability;
4. Exploration of hybrid catalytic systems combining Nb_2O_5 with photocatalytic or electrocatalytic functionalities, enabling one-pot glucose valorization under mild conditions and energy-efficient conditions.

Advancements along these avenues are anticipated to bridge the current gap between promising laboratory-scale results and scalable, economically viable, and environmentally sustainable HMF production technologies.

4. CONCLUSION

Modified niobium(V) oxide (Nb₂O₅) catalysts have emerged as highly promising materials for the selective conversion of biomass-derived carbohydrates, particularly fructose and glucose, into 5-hydroxymethylfurfural (HMF). The intrinsic Brønsted and Lewis acidity of Nb₂O₅, when rationally tuned through doping, nanostructuring, or hybridization with porous supports, can significantly enhance HMF yields while minimizing by-products.

However, key challenges, including acid site optimization, catalyst deactivation, and mechanistic uncertainty, must still be addressed to facilitate industrial-scale application. The scope for advancing research remains extensive. Primarily, a major direction for future research is based on the utilization of advanced in situ and real-time reaction monitoring techniques, which are crucial for revealing the behavior of catalysts and identifying intermediates compounds, which are fundamental for informed catalyst development. Second, the exploration of green and renewable solvent systems may enhance process sustainability and product recovery. Third, the engineering of multifunctional catalysts with dual acid-base or redox properties could enable the efficient conversion of more complex biomass substrates beyond monosaccharides. The application of computational simulations is anticipated to streamline the identification of efficient catalyst formulations and enable more precise performance forecasting of niobium(V) oxide catalysts.

Finally, future niobium(V) oxide catalyst studies should emphasize durability, reusability, and techno-economic feasibility under realistic processing conditions to narrow the gap between experimental research and industrial application. These approaches enable the enhancement of resilient, selective, and eco-efficient Nb₂O₅ catalysts, facilitating the transition toward sustainable chemical synthesis.

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