Sustainable Conversion of CO_2 to Methanol via Catalytic Hydrogenation

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Abstract: Given the growing concern about carbon dioxide (CO2) emissions and their environmental implications, the search for alternatives for reusing this gas has gained prominence, with methanol production being a route that holds great potential given the versatility of this chemical compound. This study explored the various strategies for converting CO2 into methanol, with a particular focus on catalytic hydrogenation and the potential of rhenium- and titanium-based catalysts in this process. To this end, an in-depth analysis of relevant academic papers was conducted, which investigated both the reaction conditions and the effectiveness of different catalysts in the transformation of carbon dioxide. The comparative evaluation of the data obtained, consolidated in theoretical frameworks that discuss the application of supercritical flow systems and the performance of innovative catalysts, revealed the particularities of the different catalytic approaches and the variables that influence selectivity and conversion yield. It is noteworthy that using green hydrogen, which comes from renewable sources, can maximize the environmental benefits of the process. This reinforces the viability of this approach in a circular economy context.

Catalytic hydrogenation of CO_2, especially when performed under supercritical flow conditions and with advanced catalysts such as $ReOx/TiO_2$, is emerging as a promising avenue for producing methanol sustainably. It offers high selectivity, operational stability, and the potential for integration into large-scale industrial processes. However, optimizing these systems still requires further research, both in the development of new catalysts and in adapting technologies for competitive and environmentally safe commercial applications.

Keywords: Catalytic Hydrogenation; Carbon Dioxide; Methanol; Rhenium Catalysts;

1. Introduction

The steady increase in carbon dioxide (CO2) emissions from industry and the intense use of fossil fuels has generated significant environmental concerns. The consequences are already evident in the worsening of climate change, which has driven the search for effective and economically viable solutions. Currently, two main strategies are widely discussed: carbon capture and storage (CCS) and carbon capture and utilization (CCU). While CCS seeks to store CO2 underground, CCU is even more interesting because it allows for The conversion of gas into useful products for various sectors, such as methanol.

Methanol is gaining importance due to its great versatility, used in the manufacture of plastics, diluents, and several other essential items. However, most of the methanol currently produced comes from the reforming of natural gas, a process that, ironically, emits more CO2. According to Gothe et al. (2020),
converting CO2 into methanol is one of the most efficient strategies for carbon recovery, enabling the integration of this compound into the circular economy and reducing its presence in the atmosphere.

This perspective is reinforced by the work of Olah et al. (2009), who introduced the concept of the *Methanol Economy*, highlighting methanol as a sustainable alternative to fossil fuels. Similarly, Aresta et al. (2014) emphasize the role of catalytic processes for CO_2 valorization in creating a more sustainable chemical industry. Moreover, Dimitriou et al. (2015) demonstrate that methanol from renewable sources can present a favorable life-cycle assessment, reducing emissions and energy dependence. Therefore, directly transforming CO2 into methanol, using hydrogen from renewable sources, represents an important innovation for reducing pollution and, while simultaneously adding economic and industrial value.

Among the CCU options, the hydrogenation of CO2 to methanol has gained prominence because it can be applied on a large scale. However, this approach still presents challenges, such as the need for efficient catalysts that ensure high selectivity for methanol while minimizing the formation of undesirable byproducts such as carbon monoxide (CO) and methane (CH4). Catalysts based on rhenium oxide supported on titanium dioxide (ReOx/TiO2) offer superior performance compared to traditional copper catalysts (CuO/ZnO), ensuring greater efficiency and stability in CO2 conversion [1]. This improvement in selectivity and process yield reinforces the potential of this approach for the chemical and energy industries.

This study seeks to deepen the understanding of the selective transformation of CO2 to methanol through catalytic hydrogenation in supercritical flow systems. The research will analyze the influence of different reaction variables and the effectiveness of new catalysts, aiming to contribute to the development of more sustainable and economically viable processes.

The hope is that the results will encourage the use of new technologies, reducing carbon release and accelerating the transition to a cleaner industrial system.

2.1. Overview

In recent years, methanol production from CO2 has attracted considerable interest, driven by the "power-to-fuel" concept. The "power-to-fuel" concept seeks to utilize carbon dioxide as a raw material for the composition and production of fuels and chemical products, representing an alternative that can aggregate and diversify the energy matrix, reduce dependence on fossil fuels, and contribute to reducing greenhouse gas emissions. The scientific article "Methanol Production by CO2 Hydrogenation: Analysis and Simulation of Reactor Performance" by Leonzio et al. (2019) discusses the vision of methanol production by CO2 hydrogenation, emphasizing its potential in this scenario.

Hydrogen (H2) production plays a fundamental role in the conversion of CO2 to methanol. Green hydrogen, produced from renewable sources such as water electrolysis using wind or solar energy, is an extremely favorable path to making the process even more sustainable. The use of green hydrogen significantly reduces emissions associated with methanol production compared to hydrogen obtained from fossil fuels.

To understand the feasibility of this transformation, it is necessary to investigate the

outperform conventional copper and zinc catalysts (CuO/ZnO) [2]. Furthermore, variables such as temperature, pressure, and molar ratio of reactants significantly influence selectivity and reaction performance.

In addition to reducing the industrial carbon footprint, the conversion of CO2 to methanol offers significant economic advantages. Replacing fossil fuel-based processes can significantly reduce carbon emissions. However, the cost of infrastructure and the availability of green hydrogen remain obstacles. Even so, the global trend toward sustainable solutions points to this technology as strategic for a cleaner and more efficient energy future.

2.2. Emerging Technologies in CO2 Hydrogenation

Catalytic CO2 hydrogenation represents one of the most relevant strategies for sustainable methanol production. Among the main CO2 conversion routes, electrochemical reduction

Different technological paths available, including the use of catalysts that accelerate the reaction and the ideal conditions for it to occur efficiently. Process efficiency is directly associated with the type of catalysts used and the specific system conditions. Recent studies indicate that rhenium oxide-based catalysts
supported on titanium dioxide (ReOx/TiO2) can

stands out.

It operates under mild conditions and allows for fine selectivity control. However, it presents efficiency challenges, energy consumption and high electrode costs. Photocatalytic reduction, which uses light as an energy source, is promising from an environmental perspective. However, it is still limited to laboratory scale. Homogeneous catalysis offers high selectivity and molecular control, but its separation and recovery of catalysts is complex. Heterogeneous catalysis is more compatible with industrial applications, especially on a large scale.

Heterogeneous catalytic hydrogenation in supercritical flow has shown great potential compared to other approaches. This route, as demonstrated in the research, combines the advantages of high conversion efficiency with the possibility of operating under continuous conditions. We also see that ReOx/TiO2 catalysts have stood out for their superior selectivity and stability during the process. Furthermore, the use of supercritical flow systems increases the interaction between the reactants and the catalytic surface, improving yield and reducing unwanted byproducts.

2.3. Steps and Conditions in Catalytic Hydrogenation

The conversion of CO_2 to methanol by catalytic hydrogenation occurs through fundamental steps: adsorption of CO_2 and H_2 on the catalyst surface. Activation and dissociation of the molecules, generally facilitated by temperatures between 180°C and 270°C and pressures of 30 to 100 bar. Chemical reaction at the active sites of the catalyst, leading to the formation of methanol. Desorption of the final product, allowing its removal and purification.

Typical equipment includes fixed-bed tubular reactors or continuous-flow reactors operating in a supercritical regime. Membrane reactors, which have arrangements that would allow the removal of products, such as CH_3OH and H_2O, from the reaction environment, offer great potential, improving yield and reducing costs. Technical challenges involve the stability of catalysts under high pressure and temperature, as well as the sustainable supply of hydrogen.

2.4. Materials and Methods

This research adopts an exploratory and evaluative approach, aiming to analyze possible pathways for transforming carbon dioxide into methanol, focusing on catalytic hydrogenation, using a systematic literature review on carbon dioxide (CO_2) conversion. The purpose is to analyze the technological advances, challenges, and various reaction conditions involved in this process, with an emphasis on the use of rhenium- and titanium-based catalysts.

Three academic theses were analyzed as main data sources: Gothe (2021), which addresses the valorization of supercritical CO_2 in methanol using ReO_x/TiO_2 catalysts; Guimarães (2023), who investigated CO_2-assisted methanol conversion using V/H-ZSM-5 catalysts; and Nogueira (2014), who discussed the synthesis and application of niobium-modified TiO_2 catalysts.

The material was analyzed comparatively, considering aspects such as catalyst efficacy, selectivity, conversion, reaction conditions (pressure, temperature, reactant ratio), and technical feasibility. The results were verified based on the theory presented in the theoretical framework of this work, particularly the research by Gothe et al. (2020) and Guimarães (2019), who discussed the benefits of using supercritical flow systems and alternative catalysts in sustainable methanol production.

The preparation of the catalysts used in the studies analyzed involved different methodologies, such as the wet impregnation of metal oxides on supports, such as the impregnation of NH_4VO_3 (ammonium metavanadate) on H-ZSM-5 (zeolite) to obtain V/H-ZSM-5 catalysts (a formation that would function as a complex where the vanadium compounds act as active catalysts and the zeolite as a support). Another technique employed was the Pechini method for the synthesis of catalysts based on niobium-modified titanium dioxide. These materials were characterized using several techniques, including X-ray diffraction (XRD) for analysis of crystalline phases, UV-Vis absorption spectroscopy for evaluating optical properties, and scanning electron microscopy (SEM) for morphological analysis.

CO_2-to-methanol conversion experiments were conducted under varying reaction conditions. Some studies employed supercritical flow systems, which allow operation at high pressures and temperatures, optimizing the interaction
between the reactants and the catalyst. Typical reaction conditions included temperatures between 180°C and 270°C and pressures between 30 and 100 bar, with CO_2:H_2 molar ratios of 1:3 or 1:4. Analysis of the reaction products was performed using techniques such as gas chromatography, allowing quantification of methanol and any byproducts formed.

2.5. Results and Discussion

Based on the literature review, significant advances in the conversion of CO_2 to methanol through catalytic hydrogenation were identified. Recent studies have demonstrated a growing trend toward the development of more selective and stable catalysts, aiming for greater process yield and sustainability.

Gothe et al. (2020) highlights that the use of supercritical systems, combined with catalysts such as ReO_x/TiO_2, allows achieving conversions above 40% and selectivity close to 98% for methanol under ideal temperature and pressure conditions. These results are superior to those obtained with conventional catalysts such as CuO/ZnO, which tend to present lower thermal stability and formation of byproducts, such as CO and CH_4.

Furthermore, Guimarães (2019) highlights that the morphology and dispersion of rhenium oxide in Titanium dioxide supports directly influence catalytic activity, promoting greater CO_2 adsorption and facilitating its conversion to methanol. This finding reinforces the importance of controlling catalyst synthesis parameters for process optimization.

Table 1 summarizes the main operating conditions used in the studies analyzed, highlighting the temperature ranges (200–270 °C), pressure (50–100 bar), and the CO_2:H_2 molar ratio of 1:3, which proved most efficient for the desired reaction.

Table 1. Summary of efficient operating conditions

Catalisador	Condições (T, P, razão CO_2:H_2)	Conversão	Seletividade	Observações
ReOx/TiO_2	200–270 °C; 50–100 bar; 1:3	>40%	~98%	Alta estabilidade em regime supercrítico
CuO/ZnO/Al_2O_3	200–270 °C; 50–80 bar; 1:3	35–45%	70–80%	Formação de CO e CH_4; menor estabilidade
V/H-ZSM-5	200–250 °C; 40–70 bar; 1:4	30–38%	60–70%	Boa dispersão, mas menor seletividade
Nb–TiO_2	180–250 °C; 40–90 bar; 1:3	32–40%	75–85%	Estabilidade intermediária

Summary of efficient operating conditions for the conversion of CO_2 to methanol by catalytic hydrogenation, highlighting the most commonly used catalysts and the optimized conditions found in the analyzed studies.

Yields in the range of 65–85% were observed under the most optimized conditions, with this range being declared for ReOx/TiO_2 catalysts with the highest required product content, methanol. This maintains the yield of traditional catalysts, but contains a greater amount of byproducts.

Catalysts based on rhenium oxide supported on titanium dioxide (ReOx/TiO_2), as highlighted by Gothe et al. (2020), demonstrated conversions exceeding 40% and selectivity approaching 98% for methanol under supercritical flow conditions, indicating great potential for more efficient processes.

The morphology and dispersion of rhenium oxide on the titanium dioxide support are critical factors that influence the catalytic activity of these

Typical reaction times range from 2 to 8 hours, depending on the type of reactor and catalytic system. ReOx/TiO_2 catalysts are used for shorter reaction times, as analyzed in the studies.

Copper (Cu)-based catalysts, often combined with zinc (ZnO) and alumina (Al_2O_3), while maintaining the same yield as the catalysts studied, still lack the required selectivity. This is mainly due to their inability to withstand supercritical flow, resulting in loss of quality during the process and increasing the amount of byproducts produced.

materials, promoting greater CO_2 adsorption and facilitating its conversion to methanol [1].

Another relevant aspect observed in the articles is the process's contribution to reducing carbon emissions. In his thesis, Guimarães (2019) highlights that replacing the conventional methanol route with the CO_2-based route allows for a reduction of up to 70% in emissions associated with the molecule's production, making this technology particularly strategic in light of global climate commitments.

Despite this, the studies highlight some limitations. Most research is still conducted on a laboratory scale, requiring advances in process engineering and infrastructure to make it viable for large-scale industrial applications. Even so, the convergence of results obtained by different authors points to a favorable path for the use of CO_2 as an input and for the advancement of clean technologies in the chemical industry.

Thus, the data gathered in this review demonstrate that the hydrogenation of CO_2 in supercritical flow systems using advanced catalysts represents a technically viable and environmentally advantageous strategy. Investing in further studies of these studies may be the way to accelerate the Development of

observed in catalyst development and the optimization of reaction conditions.

Catalysts based on rhenium dioxide supported on titanium oxide demonstrate high selectivity for methanol and good catalytic activity in supercritical flow systems. These results corroborate the importance of developing efficient catalysts for the conversion of CO2 to methanol, as discussed by Guimarães (2023).

The use of green hydrogen, produced from renewable sources, is essential to ensure the sustainability of the methanol production process from CO2, which also aligns with the "power-to-fuel" concept.

Despite the advances, challenges remain to be overcome for the large-scale implementation of methanol production from CO2. Process optimization, production cost reduction, and the development of even more efficient catalysts are

industrial processes that combine efficiency, sustainability, and innovation.

2.6. Final Considerations

An analysis of the scientific literature reveals the potential of converting CO2 to methanol as an advantageous strategy for reducing greenhouse gas emissions and producing a valuable fuel. The catalytic hydrogenation of CO2 stands out as a very convenient route, with significant advanc

areas that require further research.

Future studies should focus on deepening knowledge of reaction mechanisms, exploring new catalytic materials, and developing more efficient and cost-effective green hydrogen production technologies. Furthermore, life cycle analyses and detailed economic assessments are crucial to determining the feasibility and environmental impact of methanol production from CO2 on an industrial scale.

In conclusion, the conversion of CO2 to methanol represents a choice that could potentially deliver immensely satisfactory and surprising results for the production of cleaner fuels and the reduction of emissions. The results represented in the analyzed studies demonstrate the potential of these technologies and encourage continued research and development in this area.

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