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Investigating the Efficacy of H-Beta Zeolite Catalyst Modified by Zirconium Nanoparticles in Direct LPG Synthesis from Carbon Dioxide

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1. ABSTRACT

Carbon dioxide plays a significant role in world climate change and is a prominent byproduct of various human activities, notably industrial processes. Current trends in the energy sector highlight the importance of CO_2 valorization, particularly its conversion into valuable chemicals or fuels. This study investigates the direct hydrogenation of carbon dioxide for the production of liquefied petroleum gas (LPG). The investigation employs a beta zeolite catalyst further enhanced with zirconium nanoparticles. The experimentation was conducted in a fixed bed reactor, to get any idea about critical parameters like reaction temperature and residence time. The findings indicate that the optimal conditions for liquid gas production are 380 °C and 12 $g.h.mol^{-1}$ for reactor temperature and residence time respectively. Experimental observations revealed a CO_2 conversion rate of 29.2% and a selectivity of 39.3% towards hydrocarbon products under the designated experimental parameters. Furthermore, the characterization of products stream was carried out and showed a distribution of 10.2%, 66.2%, and 15.2% for ethane, LPG, and C_2^+ hydrocarbons derivatives, respectively.

Analysis from the FTIR analysis using adsorption of pyridine on the Zr/zeolite-β catalyst showed the formation of new Brønsted and Lewis acid sites. These acid sites are crucial in facilitating the chemical conversion process of carbon dioxide. The evaluated catalyst exhibited excellent stability, maintaining its activity for a prolonged duration of 100 hours without any observable deactivation. Throughout this period, the CO_2 conversion rate remained remarkably constant at approximately 20.5%.

Keywords: LPG Synthesis, Carbon Dioxide Hydrogenation, Acidity, Deactivation, Selectivity

2. INTRODUCTION

The emission of greenhouse gases, particularly carbon dioxide (CO2), has emerged a significant environmental concern due to its detrimental effects on climate change, world temperature rise, and human health.

These gases act like a blanket on earh surface- as heat trap-, absorbing infrared radiation of sun which in turn cause global warming.

Studies have consistently demonstrated that greenhouse gas emissions, mainly CO2, are the primary drivers of climate change, leading to an average global temperature increase of 1°C in the past two decades [1, 2]. These alterations have far-reaching consequences for societies, environment, and public health in the world. Recent research has focused on utilizing CO2 for the production of fuels such as methanol, methane, and even gasoline. This approach holds promise in reducing reliance on fossil fuels and transitioning towards more sustainable energy sources [3]. The production of liquefied gas from CO2 can lead to job creation and the development of novel technologies. Additionally, this process can contribute to mitigating air pollution stemming from the combustion of fossil fuels. Employing CO2 as a feedstock can help to reduce fossil fuel consumption and safeguard the environment.

However, despite of these beneifts, this technology is associated with some challenges too.

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For example, the production cost of liquefied gas from CO2 is relatively high. Consequently, the development of a more efficient technology at a reduced cost is really crucial for the widespread adoption of this process [4, 5]. In addition to that, establishing appropriate infrastructure for the storage and transportation of CO2 liquefied gas would be essential too. Investigation into the Synthesis of Liquefied Petroleum Gas (LPG) via CO2 Hydrogenation using Zirconium-Modified H-Beta Zeolite Catalyst. This research delves into the synthesis of Liquefied Petroleum Gas (LPG) through the hydrogenation of carbon dioxide (CO2) employing a zirconium-modified H-Beta zeolite catalyst. The study utilizes a fixed-bed reactor to conduct all reactions and systematically examines the influence of operational parameters, including residence time, temperature, and feedstock. To enhance selectivity and conversion percentage, the H-Beta zeolite is modified with zirconium nanoparticles. Additionally, the catalyst's stability performance is thoroughly evaluated.

3. MATERIALS AND METHODS

3.1 Synthesis of Catalyst

Ion exchange method was employed for the modification of Si-Beta with zirconium. Appropriate amounts of Si-Beta and zirconium(IV) dichloride were ground to fine powder to obtain a Zr-containing zeolite mixture. Subsequently, the mixture was calcined at 550°C for 6 hours with a heating rate of 2°C/min to yield Zr-Beta.

3.2 Catalyst Characterization

X-ray diffraction (XRD) using a Bruker D8 model was employed to investigate the catalyst's structure and crystallinity. Copper Kα radiation (λ Kα = 1.78897 Å) was utilized under conditions of 40 kV and 30 mA. Surface area and pore volume of the catalyst were measured using the BET and BJH theories based on nitrogen gas adsorption-desorption at 77 K. FT-IR analysis was performed using a PerkinElmer spectrometer equipped with a transmission cell. Transmission Electron Microscopy (TEM) analysis using a JEOL JEM-2200FS instrument was employed to characterize the structure and morphology of the synthesized sample.

4. RESULTS AND DISCUSSION

4.1. Residence Time Effect

Figure 1 illustrates the influence of residence time on CO2 hydrogenation to LPG at a temperature of 380 °C and a pressure of 5 bar. Extending the residence time up to 12 g·h·mol⁻¹ boosts the CO_2 conversion percentage from 11.2% to 29.2% and the carbon monoxide selectivity from 53.8% to 66.5%. While longer residence times favor the CO_2 conversion percentage, they are detrimental to the RWGS reaction.

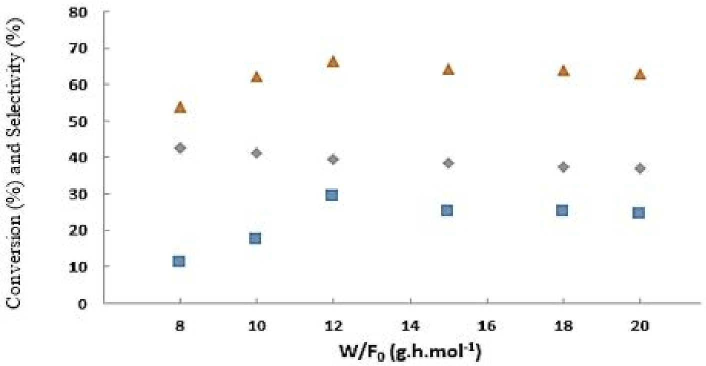

Figure 1. Effect of residence time on CO2 conversion and selectivity

4.2. Temperature Effect

The conversion of carbon dioxide to LPG was evaluated at temperatures ranging from 350°C to 450°C, with a residence time of 12 g.h.mol⁻¹ and a pressure of 5 bar. As an evident from Figure 2, both the CO_2 conversion percentage and CO selectivity increase with increasing reaction temperature. This behavior is attributed to the exothermic nature of the RWGS reaction. These findings are consistent with previous studies on CO selectivity under various reaction conditions. With increasing temperature up to 380°C, the conversion percentage rises from 18.6% to 29.2%, aligning with the exothermic nature of this reaction. Beyond this temperature, the increase in CO_2 conversion percentage exhibits minimal changes.

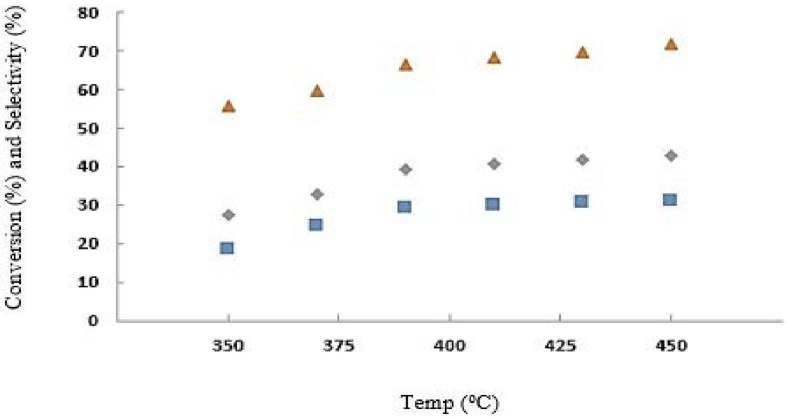

Figure 2. Effect of residence time on CO2 conversion and selectivity

5. CONCLUSION

The alarming rise in CO_2 emissions into the atmosphere and the threat it poses to humanity and the environment are significant concerns. Additionally, the depletion of fossil fuel reserves, coupled with the escalating global energy demand, presents a formidable challenge. Therefore, converting CO_2 into fuel offers a promising solution to mitigate global warming caused by the increasing CO2 concentration in the atmosphere and address the world's high energy demand. In this study, the hydrogenation of carbon dioxide to produce LPG over a Zr/Zeolite-β catalyst was investigated. Various factors influencing catalytic performance, including temperature, residence time, and CO addition, were examined. The results demonstrated that increasing the reaction temperature enhanced CO2 conversion but also elevated CO selectivity. Therefore, the optimal temperature should be carefully selected to maximize CO_2 conversion while minimizing CO production. Prolonging the residence time led to an increase in CO_2 conversion but could also promote side reactions. The optimal conditions for maximizing CO_2 conversion and LPG selectivity were determined to be 380°C and 12 g.h.mol-1, respectively).

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