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# The Impact of Bifunctional Catalyst Synthesis Method on Methanol and Dimethyl Ether Production from CO2 and H2

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A B S T R A C T

*Indonesia has initiated a zero-carbon emission plan; one strategy is to replace Liquid Petroleum Gas (LPG) with eco-friendly fuels like Dimethyl Ether (DME). However, high Operational Expenditure (OPEX) for CO2 conversion technology poses a challenge. This research aims to address these techno-economic barriers by examining how catalyst synthesis methods, specifically Ultrasonic (US) and coprecipitation (CP), impact the performance of the bifunctional catalyst Cu/ZnO/Zr/Al2O3 – H+ Zeolite Socony Mobil-5 (CZZA-HZSM-5) in DME synthesis. The catalysts are characterized using the Brunauer-Emmett-Teller (BET) method and tested in a fixed-bed reactor at 240°C and 27.6 bar, followed by a bubble reactor containing methanol. Gas Chromatography-Mass Spectrometry (GC-MS) is used for analysis. The US method produces catalysts with higher surface area, pore volume, and average pore diameter than the CP method, with values of 45.93 m²/g, 0.3822 cc/g, and 1.6646 nm, respectively. Correspondingly, the US catalyst shows higher CO2 conversion and methanol yield, at 13.3% and 59.7%. DME as the final product is undetected in GC-MS analysis, likely due to differences in HZSM5 specifications, high reaction rates, and ΔG values above 1. This study enhances understanding of how catalyst synthesis methods affect CO2 conversion efficiency, crucial for developing sustainable fuel alternatives.*

## INTRODUCTION

At the beginning of 2022, the Intergovernmental Panel on Climate Change (IPCC) published a report delineating the global climate emergency. The report asserts that human activities affect the current climate crisis due to the massive production of greenhouse gases, especially CO2. This revelation underscores the urgent need for innovative research and strategies to mitigate the impact of these emissions and steer us toward a more sustainable future [1]. Globally, the world is competing to devise carbon emission reduction strategies to achieve zero carbon emissions, including Indonesia, which plans to realize this by 2060 [2]. Indonesia is transitioning to more eco-friendly energy solutions by initiating a program to increase the use of DME as a substitute for LPG in the domestic fuel market. DME can be synthesized from carbon emissions, thus contributing to carbon reduction efforts. However, the adoption of DME faces challenges due to economic and technological factors, especially the significant operational costs associated with electricity usage and CO2 conversion technology. As a result, the process of producing DME as a fuel option has not shown a positive financial outlook when considering the present technology and market trends [3]. Many active research efforts are underway to develop methods for DME production. One such method is the environmentally friendly indirect approach, which utilizes CO2 as a feedstock. This method involves two distinct reactions: first, converting CO2 into hydrogen, and second, removing water from methanol.

Consequently, a bifunctional catalyst is employed, capable of accelerating both reactions. This method actively reduces carbon emissions and offers a viable option for turning $CO_2$, a greenhouse gas, into something valuable [4].

Bi-functional catalysts have been extensively researched and developed due to their efficiency and effectiveness. In practice, copper (Cu) catalysts are commonly used, often supplemented with other metals to enhance performance. The catalyst composition known as $Cu/ZnO/Al_2O_3$ (CZA) is used and has been improved by adding zirconium, thus creating a new, more effective catalyst called $Cu/ZnO/Zr/Al_2O_3$ (CZZA). Scientists typically synthesize these bi-functional catalysts using the co-precipitation method, which provides precise control over the catalyst's properties and optimizes its effectiveness in various chemical reactions [5], [6], [7]. The research conducted on CZZA has successfully pinpointed the superior performance of the CZZA catalyst in synthesizing methanol and DME more effectively than the CZA catalyst. The methanol yield using the CZZA catalyst reaches 12.4%[5], which is higher than the yield obtained using the CZA catalyst (3.7%) [8].

It has also recognized a drawback: CZZA stability decreased significantly during DME synthesis. This decline was attributed to decreased BET surface area and increased coking in the HZSM-5 catalyst, leading to deactivation during DME synthesis via $CO_2$ hydrogenation [5]. Achieving high-quality and abundant DME production necessitates a process that ensures high $CO_2$ conversion, selective DME formation, and substantial DME yield. Improving catalyst optimization is a crucial approach to facilitate the large-scale manufacturing of DME as a fuel, focusing on enhancing its economic and technological viability. With the same OPEX and DME synthesis operating conditions, an optimal catalyst can produce more products, making the process more economical.

Therefore, this research seeks to support carbon reduction initiatives that align with the current climate situation, development plans, and regulations in Indonesia and globally.

This study is focused on DME implementation as an alternative to LPG by improving the bi-functional catalyst used in the synthesis of DME from $CO_2$—a contributor to greenhouse gas emissions [9]. There are four methods commonly used in catalyst production: ultrasonic (US), solution combustion (SC), solid-state (SS), and coprecipitation (CP). The US method outperforms the other methods in every aspect of characterization testing, including surface area, Cu dispersion, Cu surface area, and Cu particle size [10]. On the other hand, the CZZA catalyst is most synthesized by CP method [5].

This study explains how US methods can enhance the performance of the CZZA catalyst, both in its characterization and in the analysis of products resulting from the catalyst's activity. The characteristics include surface area, pore volume, pore distribution, adsorption, desorption, and crystal shape, while the activity is represented by $CO_2$ conversion, methanol selectivity, methanol yield, and DME production. The results can enhance the understanding of how catalyst synthesis methods affect $CO_2$ conversion efficiency, which is crucial for developing sustainable fuel alternatives.

## METHODS

The equipment used in this research includes a Fixed-bed tubular reactor for conducting catalytic reactions and a Bubble Reactor for contacting the product gas with its solvent. The schematic can be seen in Figure 1.

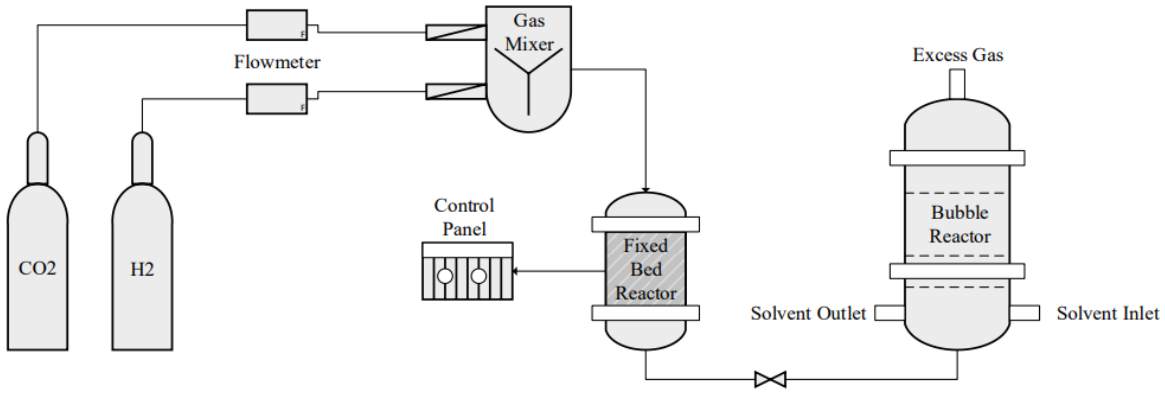


**Figure 1.** Research Apparatus Scheme

The research stages consist of catalyst preparation, catalyst characteristic testing, reactor construction, catalyst activity testing, analysis of catalyst activity results, and reporting. Catalysts are prepared using US and CP methods.

In the US method, the composition mirrors previous research [11], with a molar ratio of Cu:Zn:Al:Zr at 43.7% Cu, 43.6% Zn, 9.72% Al, and 3.0% Zr sourced from respective nitrate solids. Following this, the mixture is dissolved in 500mL of Deionized water (DI water). Both the metal nitrate and 2 M sodium carbonate solutions are added dropwise to preheated DI water (65-70°C) while being stirred at 600 RPM until the pH reaches 7.0. Subsequently, the solution container is immersed in an ultrasonic device filled with water for 2 hours. Following this step, the solution is stirred at 400 RPM and heated to 70°C for 30 minutes. The resulting precipitate is then filtered, washed with warm DI water, and dried overnight at 120°C. Finally, the precipitate undergoes calcination at 600°C for 4 hours [10], [12].

The solution with same composition also processed using CP method. This composition is dissolved in 500 mL of Deionized water (DI water). The metal nitrate solution and 2 M sodium carbonate solution are simultaneously added dropwise with preheated DI water at 65-70°C, while stirring continuously at 400 RPM to maintain a pH range of 6.5-7.0. Upon completion of dripping, the pH is adjusted to 7.0 using sodium carbonate solution. The mixture is then stirred at 400 RPM and heated to 70°C for 30 minutes. The resulting precipitate is filtered using a Büchner funnel, washed with warm DI water, and dried overnight at 120°C. Finally, the precipitate is calcined at 600°C for 4 hours [12].

The catalyst undergoes a reduction or activation process during the catalyst activity testing. Catalyst is characterized by BET analysis. Catalyst activity testing occurs on a Fixed Reactor Bed, which is set up according to Figure 1, and GC-MS is used to analyze the DME results.

Efforts to trace and adjust the research when facing results that deviate or do not align with the literature or hypotheses are conducted by revalidating the aspects of Man, Machine, Method, and Material. The investigation determines if the researcher made errors in handling or failed to follow the available methods for the Man aspect. A leak test on the reactor represents the Machine aspect. Matching the used procedures with the available literature examines the Method aspect. Exploring the Material aspect involves matching the used materials' specifications with the required specifications. Checks on the above elements will occur during the preparation stage for each research process undertaken.

## RESULT AND DISCUSSION

BET testing evaluates the US and CP catalyst products, each with a zirconium composition of 3% mol. Table 1 displays the results of the BET tests. BET results include surface area, total pore volume, pore size, and average pore diameter, while the pore size distribution during adsorption and desorption uses the Barrett-Joyner-Halenda (BJH) method. The BET and BJH methods produce different pore volume values. BET uses a single-point volume as the pore volume value, which is the total

volume below the highest partial pressure, while BJH uses the pore volume value that falls within the pore diameter range [13]. The desired catalyst characteristics should have a substantial surface area, total pore volume, and significant pore volume size. A more considerable pore diameter will enhance the adsorption and desorption capabilities of the catalyst [14].

BET results include surface area, total pore volume, pore size, and average pore diameter, while the pore size distribution during adsorption and desorption is determined using the BJH method. The BET and BJH methods yield different pore volume measurements. In BET, the pore volume values used are from a single-point volume, which is the total volume less than the highest partial pressure, while in BJH, it is the pore volume within the range of pore diameters [13]. The pore diameter value is related to the capacity to absorb gases or fluids. The larger the pore diameter, the more expansive the pathway for fluid movement, thereby increasing the efficiency of both adsorption and desorption processes [14]. The data indicates that the largest active surface area of Cu metal resides within the US method. According to BET analysis results, the surface area value for the US method is 45.9527 $m^2/g$, whereas for the CP method, it stands at 25.3539 $m^2/g$. The catalyst made by the coprecipitation method has a surface area 44.82% smaller than that of the US method. The findings are consistent with research [10], which confirms that the US method yields the largest surface area.

**Table 1.** Results of the BET tests

| Parameter | US | CP | Song (2014) [11] | Dasiredy (2019)[10] |
|---|---|---|---|---|
| BET multi-point | | | | |
| Surface Area ($m^2/g$) | 45.9257 | 25.3539 | 123 | 117 |
| Total Pore Volume (cc/g) | 0.3822 | 0.1235 | 0.85 | - |
| Pore Size (nm) | 18.48 | 18.66 | - | 9 |
| Average Pore Diameter (nm) | 1.6646 | 0.97407 | 21.1 | - |
| BJH Adsorption Pore Size Distribution | | | | |
| Surface Area ($m^2/g$) | 31.0142 | 20.4484 | | |
| Pore Volume (cc/g) | 0.0761 | 0.0504 | | |
| Pore Diameter (nm) | 3.64685 | 8.95255 | | |
| BJH Desorption Pore Size Distribution | | | | |
| Surface Area ($m^2/g$) | 77.4611 | 31.2416 | | |
| Pore Volume (cc/g) | 0.3099 | 0.1013 | | |
| Pore Diameter (nm) | 10.1794 | 10.0458 | | |

However, the results of this study are not as significant as those of research [10]. The study found that using a lower concentration of the precipitating agent ($Na_2CO_3$) increases surface area and dispersion of Cu and decreases particle size, as indicated in reference [15]. This study utilized a $Na_2CO_3$ concentration ranging from 1 to 2 molar, in contrast to the 0.1 to 0.5 molar used in reference [16]. The $Na_2CO_3$ concentration increased to maintain the stable operating conditions necessary for precipitating the CZZA metal solution at a pH level between 6 and 7. The Zr metal in the CZZA solution needs to be dissolved with 70 mL of concentrated nitric acid, making the CZZA solution have a very low pH (1.5-2.0). The $Na_2CO_3$ concentration increased to counteract the low pH of the CZZA solution, ensuring that the precipitation process met the necessary operational conditions. As a result, the surface area produced was less than that achieved in earlier studies.

Regardless of that, the effect of the US and CP method on the results obtained is consistent with previous research [10]. The US method significantly improves surface area and particle size over conventional CP. The US method can effectively aid in integrating ZnO into Alumina, serving as an 'intermediary,' thereby ensuring extensive exposure of the total surface area [17]. Introducing ultrasonic energy into the system accelerates fluid flow through the medium and results in a more porous catalyst, thereby increasing its surface area [18].

GCMS tests were performed using pure methanol as the solvent, with US and CP samples included for analysis. The purpose of the solvent injection data was to distinguish between the methanol used as a solvent and the methanol generated by the CO2 hydrogenation reaction. The methanol solvent exhibited 99.62% purity with traces of ethanol as an impurity. Both US and CP test samples showed a larger methanol area than the methanol solvent, indicating the formation of new methanol as a reaction product. The US sample revealed a larger methanol area than the CP sample. Both samples contained detectable CO2, indicating residual CO2 that did not react, whereas the H2 feed remained undetected. DME, the final product, was not found in either sample. Table 2 shows The GCMS results.

The flowmeter used was calibrated in Standard Liters Per Minute (SLPM), allowing the calculation of each feed gas's moles using the molar volume at STP (22.4 L/mol). The results were 2.6773 moles of CO2 and 9.3704 moles of H2. This calculation aimed to establish a relationship between the methanol area and the moles of methanol. The relationship enables the calculation of methanol moles in the test samples. It was defined through Equation 1, using the area and moles of methanol data from the solvent injection in the GCMS results, revealing that a methanol chromatogram area of 13,997,036 corresponds to 12.3280 moles of methanol.

The predefined mole-to-area relationship allows the calculation of methanol content in the test samples through the difference between the test sample's total area and the solvent's area. Equation 2 determines the moles of methanol in the test samples, as shown in Table 3.

**Table 2**. GCMS Test Result

| Samples | Methanol | | Ethanol | | $CO_2$ | | Hydrogen and DME | |
|---|---|---|---|---|---|---|---|---|
| | Area | %Area | Area | %Area | Area | %Area | Area | %Area |
| Solvent | 13,997,036 | 99.62 | 53,950 | 0.38 | NA | NA | | |
| CP | 15,562,658 | 99.69 | NA | NA | 47,945 | 0.31 | NA | |
| US | 15,811,896 | 99.10 | NA | NA | 120,417 | 0.90 | | |

$$n\ Methanol\ \frac{(mL\ Methanol \times density\ Methanol)}{MR\ Methanol} \times \%Methanol = Chromatogram\ Area \quad (1)$$

$$n\ Methanol\ sample = \frac{Area\ sample}{area\ standard} \times n\ Methanol\ Standard \quad (2)$$

Methanol yield indicates the ratio between the formed methanol and the incoming feedstock, presented in percentage form. In the CO2 hydrogenation reaction, the moles of methanol that form should equal the moles of the incoming CO2 feedstock. Equation 3 determines the methanol yield, and Table 3 displays the methanol yield for each catalyst production process.

$$Y\ Methanol = \frac{n\ methanol\ sample}{n\ CO2 + n\ H2} \times 100\% \ldots (3)$$

**Table 3.** Methanol Yield

| Samples | Methanol in sample (mole) | Methanol in feed (mole) | Methanol yield (%) |
|---|---|---|---|
| CP | 1.3842 | 12.0477 | 11.5 |
| US | 1,5985 | | 13.3 |

In the ongoing reaction, the CO2 hydrogenation and Water Gas Shift reactions can consume CO2, indicating that the CO2 conversion reflects the amount of CO2 reacting in these reactions. The GCMS results show no CO gas, suggesting that the Water Gas Shift reaction does not consume CO2, and the CO2 hydrogenation reaction consumes all the CO2. Therefore, the amount of converted CO2 is equivalent to the quantity of methanol product formed in the CO2 hydrogenation reaction. The detected CO2 chromatogram area in the feed merely shows unconverted CO2, meaning its presence in the test sample has no impact on the CO2 conversion value. Equation 4 yields the CO2 conversion value for the test sample, and Table 4 presents this CO2 conversion data.

$$X\ CO2 = \frac{n\ CO2\ converted}{n\ CO2\ feed} \times 100\% \quad (4)$$

**Table 4.** CO2 conversion

| Samples | $CO_2$ in sample (mole) | $CO_2$ in feed (mole) | X $CO_2$ (%) |
|---|---|---|---|
| CP | 1.3842 | 2.6773 | 51.7 |
| US | 1.5985 | | 59.7 |

The GCMS testing results do not detect DME, allowing analysts to concentrate on how catalyst production affects methanol yield. Showcasing the impact of the CZZA-HZSM5 catalyst fabrication technique on DME synthesis solidifies the research's foundation. The creation of the CZZA catalyst, a bifunctional component essential for methanol production through CO2 hydrogenation, underscores the distinction in catalyst fabrication methods. Evaluating the research premise is thus possible by looking at the methanol produced. Additionally, the methanol amount formed can predict the potential volume of DME producible [5]. HZSM5, a commercial material, is responsible for forming DME and is mixed with the synthesized CZZA catalyst.

GCMS results reveal that the CZZA US catalyst generates a larger methanol area, directly resulting in more methanol production and a superior methanol yield than the CZZA CP catalyst, suggesting the CZZA US catalyst has enhanced catalytic activity. The US method's catalyst is better because it uses sonication during its creation. This process applies high pressure and temperature, leading to better crystal growth and preventing clumps. The result is a catalyst with tiny, even-sized particles, well-spread active sites, and a larger surface.

**Table 5.** Methanol Mole Calculation Results in the Test Sample

| Samples | Standard Solvent Area | Sample Reading Area | Sample Area | Methanol standard (mole) | Methanol sample (mole) |
|---|---|---|---|---|---|
| CP | 13,997,036 | 15,562,658 | 1,571,622 | 12.3820 | 1.3842 |
| US | | 15,811,896 | 1,814,950 | | 1.5985 |

Table 1 presents consistent results in surface area, pore size, and pore distribution. Sonication treatment can also reduce the crystallinity of CuO metal, thus promoting the formation of CuO-ZnO bonds, which are responsible for the formation of methanol via CO2 hydrogenation reaction [16].

Extending the aging time (slow stirring) in the precipitation treatment of the CP method can increase the intensity of the CuO-ZnO bond. However, it may also trigger the aggregation of catalyst crystals and reduce the size homogeneity of the catalyst. Integrating sonication treatment into the conventional precipitation technique addresses these shortcomings and leads to the development of an improved CZZA catalyst. Table 6 shows the comparison of the performance of the US catalyst with the performance of the CP catalyst from other research, indicating that both methanol yield and CO2 conversion show advantages for the US catalyst.

**Table 6**. Comparison of Catalyst Performance

| Parameter | This Study | | Ren, 2019 | Ren, 2018 |
|---|---|---|---|---|
| | CP | US | CZZA CP | CZA CP |
| MeOH Yield | 11.5 | 13.3 | 12.4 | 12.8 |
| $CO_2$ Conversion | 51.7 | 59.7 | 26.5 | 26-28% |

The lack of a pressure gauge requires calculating the actual reactor pressure using the ideal gas law (equation 7), estimating it at 42.4 atm. Undetected product gases due to methanol's limitations as a solvent might contribute to the pressure discrepancy, potentially resulting in a smaller mole value and a pressure below 42.4 atm.

$$\boldsymbol{P \times V = n \times R \times T} \quad (5)$$

$$\boldsymbol{P \times Q_{feed} = n_{feed-product} \times R \times T} \quad (6)$$

$$\boldsymbol{P = \frac{n_{feed-product} \times R \times T}{Q_{feed}}} \quad (7)$$

Despite efforts to adjust the operational conditions of the research to match literature that can demonstrate good product results, the GCMS results only show the presence of methanol and CO2 and do not indicate the presence of DME in the solvent. Possible reasons for DME's absence include variations in HZSM5 specifications, treatment methods, and thermodynamic limitations.

In bifunctional catalysts, HZSM5 serves to catalyze the dehydration of methanol. Therefore, the catalyst's non-detection might stem from the HZSM5's lack of optimal activity. A comparative analysis with various studies reveals that Table 7 highlights differences in the specifications of the HZSM5 used in this research compared to those used in other studies.

A variation in the Si/Al ratio does not significantly affect the outcome; research exists that employs a 27:1 ratio and successfully yields DME [15]. The higher surface area of HZSM5 enhances its ability to produce DME, providing more active sites for methanol dehydration into DME. Even with a lower surface area, HZSM5 should still facilitate the formation of DME, albeit in reduced amounts [5], [19], [20]. The significant factor is the varying acidity levels of HZSM5, which exhibits more catalytic activity than other methanol dehydration catalysts like γ-alumina due to its abundance of acid sites [15]. This unidentifiable parameter in the actual HZSM5 is the most likely alternative responsible for the absence of DME in the GCMS tests conducted in this research. This situation causes the methanol dehydration reaction to proceed without a catalyst, necessitating higher duration, pressure, and temperature, which prevents the formation of DME.

**Table 7.** Differences in the specifications of the HZSM5

| Parameter | HZSM Aktual | HZSM (Ren,2019) | Unit |
|---|---|---|---|
| Si/Al Ratio | 27:1 | 23:1 | N/A |
| Surface Area | 365 | 425 | $m^2$/gram catalyst |
| Acidity (H) | N/A | 510 | μmol/gram catalyst |

In certain studies, the HZSM5 catalyst is Ammonia-ZSM5 or Na-ZSM5, which undergoes calcination at 500°C for 5 hours and yields 15-20% DME production [5]. This study suggests that commercial HZSM5, potentially Ammonia-ZSM5 or Na-ZSM5 already calcined, may cause the absence of DME. Other research, which similarly used commercial HZSM5 and conducted calcination under similar conditions, produced a DME yield of 27% [6]. The study did not to conduct calcination on commercial HZSM5 because its Si/Al ratio was higher than that of the referenced studies [5], [6] as shown in Table 7. However, this difference might contribute to the absence of DME, highlighting the need for future research evaluations.

The values of ΔG° and ΔH° are calculated from Table 8 data, which lists the ΔG° and ΔH° values of each pure component involved in the CO2 hydrogenation reaction. Equations 8 and 9 yield a ΔG° value of 22.39 kJ/mol and a ΔH° value of -53.71 kJ/mol. For a reaction to be spontaneous, the value for ΔG° is always negative.

$$\Delta G^{\circ}_{reaction} = \Delta G^{\circ}\ product - \Delta G^{\circ}\ reactant \quad (8)$$

$$\Delta H^{\circ}_{reaction} = \Delta H^{\circ}\ product - \Delta H^{\circ}\ reactant \quad (9)$$

The pure component K value is obtained through the previously acquired ΔG° value, allowing the determination of K through Equation 1, resulting in a K value of 0.4004.

**Table 8.** Data for pure component

| Parameter | Reactant | | Product |
|---|---|---|---|
| | Methanol | Water | DME |
| $\Delta G_f^o$ (kJ/mol) | -162.3 | -228.61 | 88.7 |
| $\Delta H_f^o$ (kJ/mol) | -48.08 | -57.80 | - 43.99 |

The calculations above yield a K value of 0.4004 and a ΔG° value of 22.39 kJ/mol, indicating that the methanol dehydration reaction is not occurring spontaneously. Given the suboptimal presence of acid sites in HZSM5, the methanol dehydration reaction may proceed ineffectively, leading to the absence of DME formation.

## CONCLUSION

In conclusion, this study investigates the impact of preparation methods on catalyst performance, focusing on physical characteristics (BET and BJH) and catalytic activity (methanol yield and $CO_2$ conversion). The US method, which employs sonication treatment, yields catalysts with larger surface areas and pore volumes than those produced by the Co-precipitation (CP) method. These findings align with higher methanol yield and $CO_2$ conversion rates observed in US catalysts. Even though DME did not appear in the final product, the effects of sonication treatment are apparent in both the characterization of the catalyst and the tests of its catalytic activity. Differences in HZSM5 specifications and handling, along with lower reaction rate product values and $\Delta G^\circ$ values of 22.39 kJ/mol, contribute to the absence of detected DME.


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