Available online at website: https://journal.bcrec.id/index.php/bcrec

Bulletin of Chemical Reaction Engineering & Catalysis, 19 (4) 2024, 658-667

Research Article

Temperature and Cr-Co ratio on Production of Diethyl Ether from Ethanol Dehydration using Cr-Co/γ-Al_2O_3 Catalyst

Izza Aliyatul Muna, Firman Kurniawansyah, M. Mahfud*, Achmad Roesyadi

Department of Chemical Engineering, Institut Teknologi Sepuluh Nopember, Jl. Arif Rahman Hakim, Sukolilo, Surabaya 60111, Indonesia

Received: 28th October 2024; Revised: 2nd December 2024; Accepted: 3rd December 2024
Available online: 4th December 2024; Published regularly: December 2024

Abstract

The running down of fossil fuels and rising environmental concerns, there is an increasing emphasis on identifying eco-friendly alternative energy sources. Diethyl ether (DEE) is considered one such additive fuel that can replace fossil fuels. In this study, DEE was synthesized through the reaction dehydration of ethanol using γ-alumina catalysts impregnated with chromium and cobalt. The dehydration of ethanol performed in a fixed bed reactor using Cr-Co/γ-Al_2O_3 catalysts loading. The effect of metal ratio of Cr-Co was examined. Catalyst characterization was carried out using XRD, BET, and SEM-EDX analyses. The dehydration reaction was conducted in a fixed-bed reactor at temperatures 100 to 200 °C, with nitrogen gas flowrates between 200 and 600 mL/min as the carrier gas. The findings revealed that the increase chromium contents, and the temperature were augmenting the diethyl ether yield. And the increase of nitrogen flow rate is slightly increasing the yield of DEE and conversion of ethanol.

Keywords: Ethanol; Diethyl ether; Dehydration; γ-Alumina catalyst

How to Cite: Muna, I. A., Kurniawansyah, F., Mahfud, M., Roesyadi, A. (2024). Temperature and Cr-Co ratio on Production of Diethyl Ether from Ethanol Dehydration using Cr-Co/γ-Al_2O_3 Catalyst. *Bulletin of Chemical Reaction Engineering & Catalysis*, 19 (4), 658-667 (doi: 10.9767/bcrec.20237)

Permalink/DOI: https://doi.org/10.9767/bcrec.20237

1. Introduction

Petroleum is one of the easiest fossil fuels to transport. However, continuous consumption of petroleum without alternative fuels will lead to the depletion of its reserves. Therefore, it is essential to identify environmentally friendly alternatives to meet the demand for renewable fuels. Diethyl ether (DEE) has indeed gained attention as a promising fuel additive because of its high cetane number and excellent auto-ignition characteristics. It serves as an effective ignition booster for diesel engines [1]. DEE improves combustion efficiency, reduces emissions, and enhances engine performance, making it a valuable additive for improving fuel properties. Additionally, its relatively low boiling point and high volatility make it suitable for blending with conventional fuels, which can lead to better cold-start behavior and smoother combustion in engines [2]. It is frequently utilised as a blending additive to compensate for the limitations of ethanol fuel. DEE has been demonstrated to enhance engine performance and lower fuel consumption when added to diesel fuel [1].

The octane ratings of both ethanol and certain ethers exceed 100 [2]. Ethanol is considered a viable biofuel alternative, thanks to its octane rating of 113 and low Reid vapor pressure. However, its use as a diesel fuel additive has declined because of several challenges, such as its rapid evaporation rate and poor ignition properties. DEE can be readily synthesized by ethanol dehydration or via the Barbet process using H_2SO_4 as a homogeneous catalyst. However, this process is hindered by challenges such as

* Corresponding Author.
Email: mahfud@its.ac.id (M. Mahfud)

catalyst separation and the corrosive nature of sulfuric acid, making it costly and inefficient [3]. In contrast, DEE can be produced using heterogeneous catalysts like alumina.

Alumina (γ-Al_2O_3) is a common catalyst or catalyst support material due to its high surface area, low cost, and superior thermal stability and ability to convert ethanol to form either alkenes or ethers [4]. Various promoters, including halogens, noble metals, alkali metals, and alkaline earth metals, have been investigated to enhance catalytic activity and product selectivity [5]. Chromium, for instance, has been found to improve the selectivity of ethanol dehydration toward DEE formation [6]. At lower temperatures, cobalt-supported alumina catalysts exhibit similar ethanol conversion levels compared to pure alumina catalysts [7].

Diethyl ether and ethylene are the two products principals that can be produced by dehydrating ethanol, according to the two equation reactions below Equations (1) and (2).

$$2\ C_2H_5OH \rightarrow C_2H_5OC_2H_5 + H_2O \quad \Delta H_{298\,K} = -25.1\ kJ/mol \quad (1)$$

$$C_2H_5OH \rightarrow C_2H_4 + H_2O \quad \Delta H_{298\,K} = +44.9\ kJ/mol \quad (2)$$

The most common process includes the intermolecular dehydration of ethanol to produce diethyl ether, which is then continue to dehydrated in ethylene. Equation (1) illustrates the exothermic reaction of ethanol dehydration to diethyl ether, which is favoured at reduced temperatures [8,9]. Ethylene, on the other hand, can be formed through intramolecular dehydration, as represented by Equation (2), an endothermic reaction favoured at higher temperatures [10,11]. While numerous studies have focused on ethanol dehydration to ethylene [13-15], ethanol dehydration to DEE has received comparatively less attention [17-19]. Given the significance of DEE production and the critical role of catalysts in enhancing DEE selectivity, this study focuses on ethanol dehydration over Cr-Co/γ-Al_2O_3catalysts and their effect on DEE selectivity. Chromium, in particular, has been shown to increase the selectivity of ethanol dehydration towards diethyl ether, while cobalt-supported Al_2O_3 catalysts have demonstrated similar ethanol conversion at lower temperatures compared to Al_2O_3 alone.

The significance of diethyl ether (DEE) as a fuel additive, coupled with the essential function of catalysts in achieving optimal selectivity for DEE, underpins the focus of this research on the dehydration of ethanol. This study employs a Cr-Co/γ-Al_2O_3 catalyst to evaluate its influence on the selectivity for diethyl ether. The enhancement of catalyst characteristics through the incorporation of promoters often results in performance improvements that exceed those of the catalyst in isolation. Although a promoter may lack inherent catalytic activity, its introduction in minimal quantities to the catalyst surface or support can markedly improve attributes such as activity, selectivity, and stability, thereby highlighting the role of promoters in refining catalyst efficacy.

Chromium plays a pivotal role in creating an acidic environment that boosts the selectivity of the reaction aimed at diethyl ether synthesis. Research conducted by Srinivasan explored the γ-Al_2O_3 catalyst support modified with cobalt dispersion, revealing that the synthesis method based on strong electrostatic adsorption (SEA) significantly enhances catalyst performance. The application of Temperature Programmed Desorption Fourier Transform Infrared Mass Spectrometry (TPD-FTIR-MS) to analyze the adsorbed species, such as pyridine and CO_2, indicated that the Co-Al_2O_3 catalyst exhibited approximately 50% of the Lewis acidity found in the original γ-Al_2O_3, while demonstrating a slight increase in alkalinity. Notably, despite the reduction in acidity, the Co-Al_2O_3 catalyst maintained comparable conversion rates for both ethylene and ethanol relative to the unmodified γ-Al_2O_3, even at lower temperatures under identical experimental conditions. This observation suggests that the incorporation of cobalt enhances overall catalytic efficiency, primarily by optimizing the interplay between acidity and alkalinity, which is crucial for catalyst activity. Furthermore, the results from ME-PSD-DRIFTS indicated the possible involvement of adsorbed ethanol and ethoxide species, along with terminal and hydroxyl groups associated with the octahedral and tetrahedral configurations of aluminum in Al_2O_3 (100) and (110) surfaces, as intermediates in the transformation of ethanol into diethyl ether and ethylene [7].

The addition of both chromium and cobalt to γ-Al_2O_3 presents an intriguing subject for further study, as the simultaneous incorporation of these metals is expected to enhance the catalytic effect of γ-Al_2O_3. The ratio of chromium to cobalt in the catalyst could also influence the outcome. Therefore, the purpose of our research is to study the dehydration of ethanol reaction in a fixed-bed reactor with γ-Al_2O_3 pretreated with both Cr and Co metals. Specifically, we focus on examining the effect of different Cr-Co ratios (1:2) at various reaction temperatures (100-200 °C) and flow rates (200-600 mL/min of carrier gas).

2. Materials and Method

2.1 Preparation of Catalyst

The γ-Al_2O_3 as a support was impregnated with aqueous solutions of chromium nitrate nonahydrate ($Cr(NO_3)_3 \cdot 9H_2O$, Merck, ≥98.0%) and

cobalt nitrate hexahydrate ($Co(NO_3)_2.6H_2O$, Merck, ≥99.0%) using the incipient wetness impregnation method. The goal was to achieve a final catalyst with a 10 wt% loading of Cr-Co. The preparation steps were as follows: (1) Impregnation: The γ-Al_2O_3 powder was mixed with the salt solutions containing Co and Cr; (2) Drying: The impregnated catalysts dried at 120 °C for 12 hours; (3) Calcination: Catalysts were calcined at 550 °C during 3 hours under a nitrogen gas (N_2, Linde, 99.99%); (4) Reduction: The calcined catalysts were then reduced with hydrogen gas (H_2, Linde, 99.99%) at 600 °C for 5 hours in a tubular furnace.

The Cr-Co metal ratios were varied with three different compositions: 1:1, 1:2, and 2:1. These catalysts were labeled as Cr-Co 11 (1:1), Cr-Co 12 (1:2), and Cr-Co 21 (2:1).

2.2. Characterization of Catalyst

The crystalline phases of the catalysts analyze by X-ray diffraction (XRD) using an Xpert MPD diffractometer with Cu-Kα radiation (λ = 1.5406 Å), allowing assessment of crystallinity and phase composition. The Brunauer-Emmett-Teller (BET) method was applied to determine the surface area, average pore size, and pore volume of the catalysts, using N_2 physisorption on Autosorb IQ and Tristar II 3020. Before measurement, the catalyst samples were pre-treated under a helium (He) flow at 30 mL/min at 250 °C for 30 minutes. The analysis was conducted at -196 °C with liquid nitrogen (N_2) in a 30% nitrogen flow in helium gas. The catalyst morphology was examined using scanning electron microscopy combined with energy-dispersive X-ray spectroscopy (SEM-EDX), with an EDAX-AMETEK system for detailed elemental analysis.

2.3 The Reaction Dehydration Procedure

The dehydration reaction was performed in a fixed-bed reactor constructed from stainless steel, featuring an ¼ inch ID and 15 cm height, as illustrated in Figure 1. The measured quantities in the diethyl ether production process are the reaction conversion and the diethyl ether production yield from ethanol. As an activation parameter, the reaction conversion and diethyl ether production yield from ethanol are calculated. The measurement of % yield diethyl ether obtained use the Equation (3):

$$Yield\ (\%) = \frac{mole\ of\ DEE\ obtained}{moles\ of\ ethanol\ reacted} \times 100\% \qquad (3)$$

Firstly, 3 g of catalyst was introduced into the reactor, with quartz wool positioned on both sides to secure the catalyst. A vaporizer tank, also made of stainless steel (5 in diameter and 6 in height), equipped with a heating jacket (1000 $kg.m^2.s^{-3}$) and temperature control, was used to vaporize absolute ethanol (Merck, 99.99%). The reaction was performed at temperatures interval 100 to 200 °C, in introducing the vaporized ethanol through the bed of catalyst using flow of nitrogen rate of 200–600 mL/min. The reactor's temperature was controlled using the built-in temperature control system. The products from the reaction were condensed. Then the products analyzed by gas chromatograph (GC) with a FID detector.

3. Results and Discussion

3.1. Characterizations of Catalyst

Figure 2 illustrates the XRD patterns for both γ-Al_2O_3 and Cr-Co modified γ-Al_2O_3 catalysts. The data indicate that the diffractograms of γ-Al_2O_3 remained stable and did not undergo significant changes after the introduction of Cr and Co. The similar XRD patterns observed across all catalysts suggest that both Cr and Co metals were highly dispersed on the γ-Al_2O_3 support. The diffraction line characteristic for γ-Al_2O_3 appear at 2θ angles of 36.80°, 45.49°, and 67.02°. However, after the impregnation of Cr and Co into γ-Al_2O_3, there was a slight decrease in the peak intensities, indicating a reduction in crystallinity. This suggests that the crystallinity of γ-Al_2O_3 diminished slightly following the metal modification.

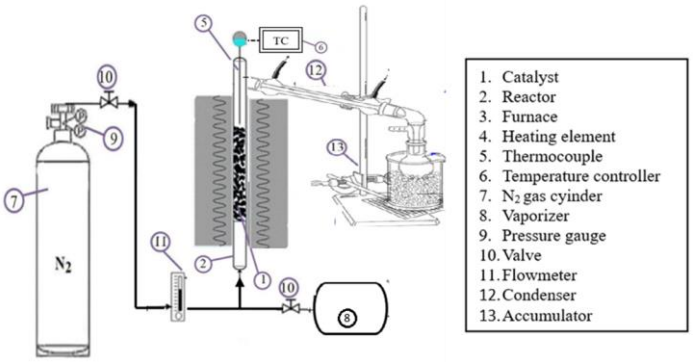

Figure 1. Apparatus scheme of fixed bed reactor.

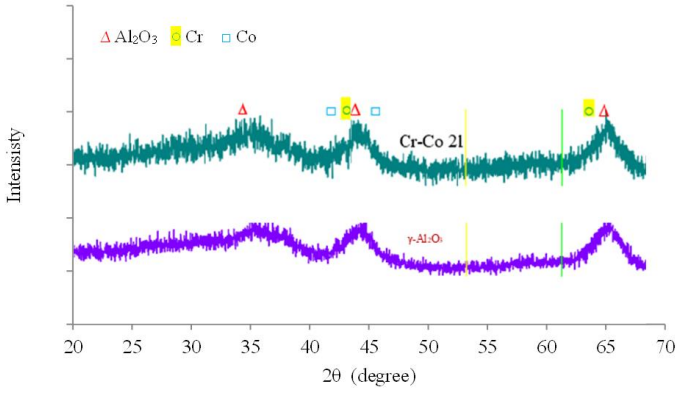

Figure 2. Comparison of XRD patterns for γ–Alumina and Cr-Co/γ-Alumina

From Table 1 shows that the surface area of γ-Al_2O_3 was 162.84 m²/g. This surface area decreased after impregnation with Cr and Co metals. The more Cr and Co added to γ-Al_2O_3, the greater the decrease in surface area, which is attributed to the blocking of alumina pores by the impregnated metals. This partly blockage indicates that the Cr and Co metals were successfully impregnated at the surface of γ-Al_2O_3 [20]. Despite the reduction in surface area, the pore diameter increased, allowing more feed molecules to access the pores [21]. Interestingly, the decrease in surface area does not negatively affect the catalyst's effectiveness. Instead, the presence of Cr and Co metals enhances the active sites of the catalyst, which is crucial for increasing the reaction rate during catalytic processes. This indicates that the active metal sites play a more significant role than surface area alone in influencing catalytic performance. The similar morphologies of the γ-Al_2O_3 and Cr-Co/γ-Al_2O_3 catalysts can be observed in Figure 3.

Chrome and cobalt were successfully impregnated into γ-Al_2O_3 and penetrated into the support pores. The content of Cr and Co in γ-Alumina reaches 10 wt.%. However, the metal weight ratios do not match the desired ratios. This result may be caused of non-uniformity of the impregnation solution during the catalyst impregnation.

3.2. Effect of Cr-Co Ratio on Diethyl Ether Yield

Prior studies indicated that the incorporation of promoters can importantly enhance diethyl ether yields by improving catalytic activity. The presence of chromium metal has been shown to favourably influence the selectivity toward diethyl ether formation. Additionally, cobalt-modified alumina catalysts can achieve ethanol conversion rates comparable to those of the original γ-Al_2O_3 catalyst under similar conditions. The findings suggest that utilizing modified γ-Al_2O_3-based catalysts, specifically those containing chromium and cobalt, is a promising approach for enhancing diethyl ether production at lower temperatures during the ethanol dehydration process. The combination of increased surface area and the catalytic properties of Cr and Co contributes to improved reaction efficiencies, making these catalysts viable candidates for industrial applications in producing diethyl ether from ethanol. The results of the experiment demonstrate the temperature effect reaction and nitrogen flow rate during the ethanol dehydration reaction are significant. Cr-Co21, with its larger BET surface area, shows that the increased surface area enhances the contact between reactants and the catalyst, thereby improving catalytic activity.

3.2.1 Effect of chrome content in Cr-Co ratio on diethyl ether yield

In Figure 4, the effect of increasing the chromium content in the Cr-Co ratio on diethyl ether (DEE) yield at various temperatures (100–200 °C) is shown. The figure illustrates that as the temperature increases, the DEE yield correspondingly rises. Furthermore, increasing the chromium content in the Cr-Co ratio significantly enhances the DEE yield, with this

Table 1. BET and EDX analysis of catalyst

Catalyst	Surface area (m^2/g)	Pore volume (cm^3/g)	Pore diameter (nm)	% weight Cr	% weight Co
γ-Al_2O_3	162.8	0.318	3.43	-	-
Cr-Co(1:1)/γ-Al_2O_3	133.5	0.229	3.90	6.86	7.44
Cr-Co(1:2)/γ-Al_2O_3	124.3	0.213	4.64	4.06	9.39
Cr-Co(2:1)/γ-Al_2O_3	91.9	0.121	3.51	8.65	4.15

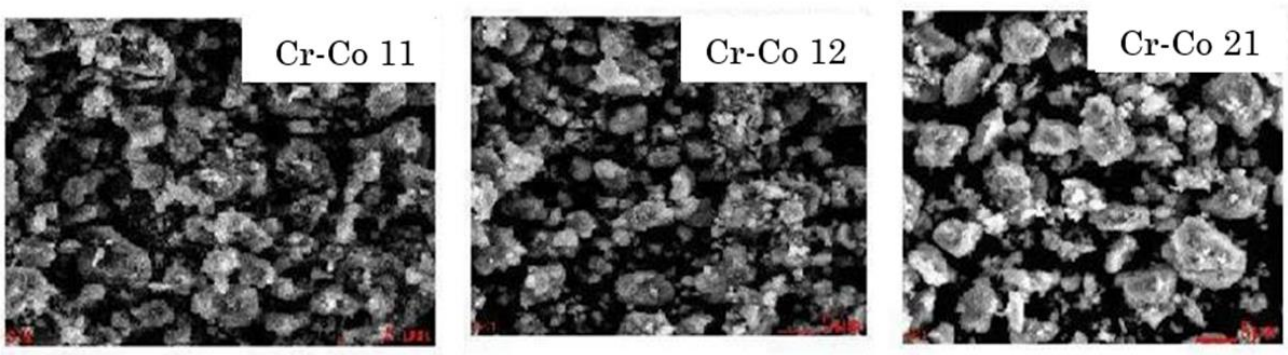

Figure 3. SEM images of all catalysts

effect becoming more pronounced at higher temperatures. The highest DEE yield observed in the study reaches 1.323 %. This indicates that both higher temperatures and increased chromium concentration in the catalyst contribute positively to maximizing the DEE production.

3.2.2 Effect of cobalt content Cr-Co ratio on diethyl ether yield

In Figure 5, the effect of increasing cobalt content in the Cr-Co ratio on diethyl ether (DEE) yield at various temperatures (100–200 °C) is depicted. The figure shows that increasing cobalt in the Cr-Co ratio results in a slight improvement in DEE yield, and this effect does not significantly change with rising temperatures. The highest DEE yield achieved with a twofold increase in cobalt content is 1.235 %. This suggests that while cobalt contributes to DEE production, its effect is less substantial compared to chromium, and temperature does not greatly influence the yield in this case.

3.3. Effect of Temperature on Diethyl Ether Yield

In Figure 6, the yield of diethyl ether increases with rising reaction temperatures, primarily due to the enhanced ethanol conversion. The reaction was carried out at temperatures interval between 100 to 200 °C. At lower reaction temperatures, all catalysts exhibited high selectivity for diethyl ether. However, as the temperature increases, the selectivity for diethyl ether diminishes. This decline is attributed to the exothermic nature of diethyl ether production (Eq. 1), which is favoured at lower temperatures. Beyond 200 °C, the selectivity for diethyl ether significantly decreases due to the endothermic nature of the dehydration of ethanol to ethylene (Equation 2), resulting in increased ethylene selectivity.

3.4. Effect of Temperature on Ethanol Conversion

The effect of temperature on ethanol conversion is significant, as higher temperatures generally lead to increased conversion rates. In the ethanol dehydration process, as the reaction temperature rises, the rate of ethanol conversion improves due to the enhanced kinetic energy of the reacting molecules. This is consistent with the principles of the Arrhenius equation, which states that increasing the temperature raises the reaction rate constant, leading to faster reactions.

At lower temperatures, such as 100 °C, ethanol conversion tends to be lower, as observed in experiments where the conversion rate was around 50.54 %. However, as the temperature increases to 200 °C, the conversion rate can reach as high as 93.12 %, as seen in the case of the Cr-Co catalyst. This demonstrates that higher reaction temperatures provide the necessary activation energy for ethanol molecules to undergo dehydration more effectively, resulting in higher conversion rates.

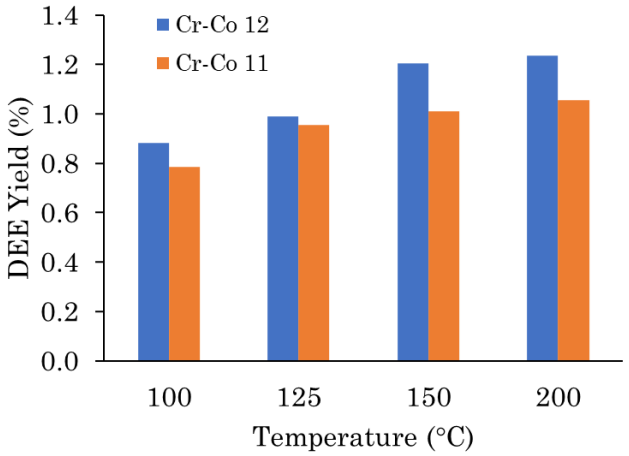

Figure 5. Effect of increasing cobalt in Cr-Co ratio on diethyl ether yield

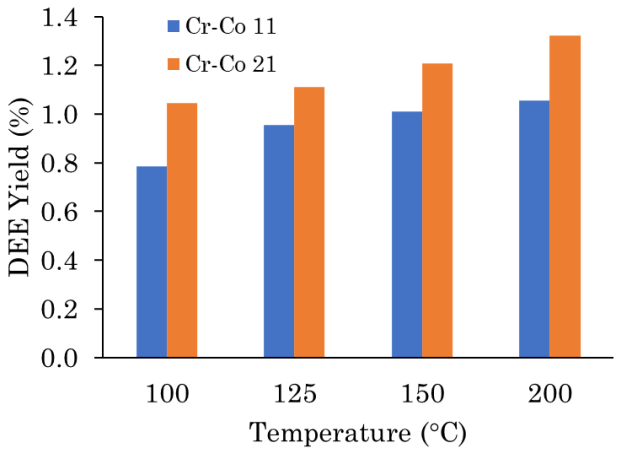

Figure 4. Effect of increasing chrome in Cr-Co ratio on diethyl ether yield

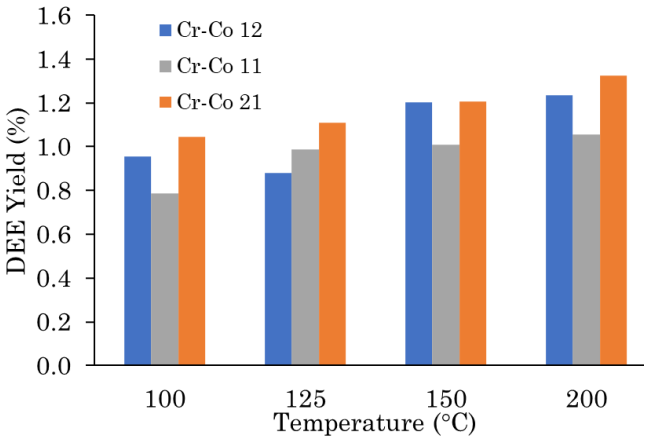

Figure 6. DEE Yield at different temperatures for different metal ratios

However, while elevated temperatures boost ethanol conversion, excessively high temperatures (above 200 °C) may shift the product selectivity from diethyl ether to ethylene, as ethylene formation becomes more thermodynamically favourable at higher temperatures [22]. Thus, optimal temperature control is crucial to maximize ethanol conversion while ensuring the desired product selectivity.

3.5. Effect of Flowrate on Ethanol Conversion

The study analysed the yield of diethyl ether and ethanol conversion under varying nitrogen flow rates and reaction temperatures. The highest diethyl ether yield of 1.32 % was observed at a nitrogen flow rate of 200 mL/min and a reaction temperature of 200 °C. Higher nitrogen flow rates (400 mL/min and 600 mL/min) resulted in lower yields due to reduced contact time between ethanol and the catalyst, limiting the reaction's progress.

Ethanol conversion also increased with higher reaction temperatures, as shown in Figure 6. The Cr-Co 1021 catalyst achieved the highest conversion rate of 93.12 % at 200 °C with a nitrogen flow of 200 mL/min. Lower nitrogen flow rates extended contact time, leading to higher ethanol conversion [23]. Conversely, at higher flow rates, such as 600 mL/min, the conversion rate decreased significantly to 33.64 % at 200 °C, highlighting the importance of balancing flow rate and temperature for optimal conversion and diethyl ether yield (Figure 8).

The yield of diethyl ether is strongly linked to ethanol conversion, with higher ethanol conversion generally leading to increased diethyl ether yields. The catalysts demonstrate high selectivity for diethyl ether at lower temperatures. However, as the reaction temperature rises, the selectivity for diethyl ether decreases due to the exothermic nature of its formation. When the temperature exceeds 200 °C, the production of ethylene becomes more dominant, which corresponds to the endothermic reactions that are favoured at higher temperatures.

3.6 A Comparison of Several Studies on Ethanol Dehydration

A comparison of several studies on ethanol dehydration highlights various approaches, catalysts, and findings, contributing to a deeper understanding of this process: (1) *Homogeneous Catalysts*: Early studies, such as those utilizing sulfuric acid in the Barbet process, focused on the use of homogeneous catalysts for ethanol dehydration. This method is effective for producing diethyl ether (DEE), but issues such as the difficulty of catalyst separation, corrosion, and high operational costs make it less desirable for industrial applications [6]; (2) *Alumina-Based Catalysts*: The use of γ-Al_2O_3 as a heterogeneous catalyst has been widely researched due to its low cost, high surface area, and thermal stability. Ethanol dehydration using γ-Al_2O_3 can yield both diethyl ether and ethylene, depending on reaction conditions, such as temperature and ethanol concentration. γ-Al_2O_3 has been shown to favour DEE formation at lower temperatures due to the exothermic nature of the reaction, while higher temperatures tend to promote ethylene production through an endothermic pathway [7]; (3) *Metal-Promoted Catalysts*: Studies involving the modification of γ-Al_2O_3 with metal promoters, such as chromium (Cr) and cobalt (Co), have demonstrated enhanced catalytic performance. Chromium, in particular, promotes the selectivity towards DEE formation by creating an acidic environment that is conducive to this reaction. Research shows that adding chromium to γ-Al_2O_3 significantly increases DEE yield, especially at higher temperatures [6]. In contrast, cobalt has been found to increase ethanol conversion at lower temperatures, but its effect on DEE yield is less pronounced compared to chromium [7]; (4) *Mixed Metal Oxides*: Some recent research has explored the use of mixed metal oxides as catalysts, where

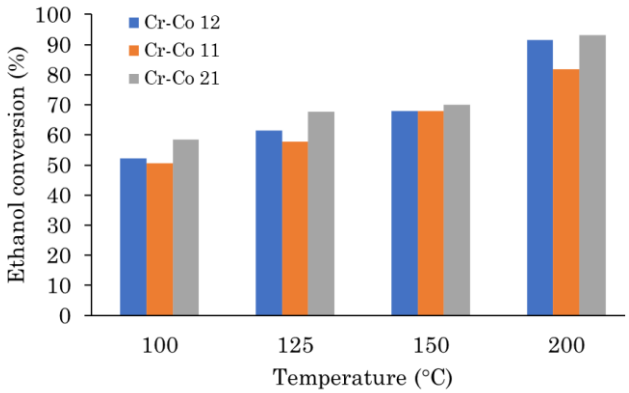

Figure 7. DEE Yield at different temperatures for different metal ratios

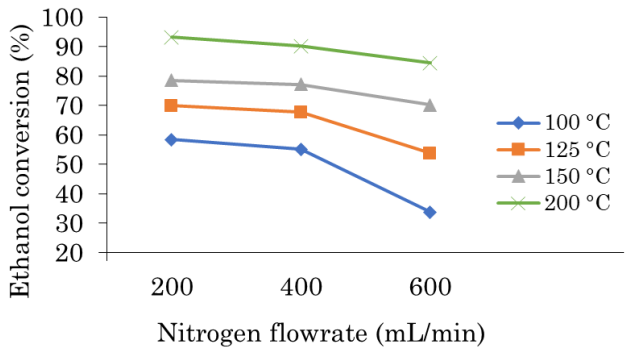

Figure 8. Ethanol conversion at different temperatures and nitrogen flowrate

the combination of two metals (e.g., Cr-Co) impregnated on γ-Al_2O_3 results in better catalytic activity and selectivity. This approach has been shown to optimize both DEE and ethylene yields depending on the metal ratio, reaction temperature, and flow rate of the carrier gas. Studies indicate that a balanced Cr-Co ratio enhances both DEE yield and catalyst stability, making it a promising method for industrial ethanol dehydration [24]; (5) *Reaction Mechanisms and Conditions*: Various studies have also focused on the mechanistic pathways of ethanol dehydration. At lower temperatures (below 200 °C), intermolecular dehydration dominates, favouring DEE formation. At higher temperatures (above 300 °C), intramolecular dehydration takes over, leading to ethylene production. These findings suggest that optimizing reaction conditions, such as temperature, pressure, and ethanol concentration, is crucial for achieving the desired product selectivity [25].

The comparison of these studies (Table 2) indicates that the choice of catalyst and reaction conditions plays a pivotal role in determining product yield and selectivity. While γ-Al_2O_3 remains a widely used catalyst, the addition of metal promoters, particularly chromium, has shown significant potential in enhancing DEE production. Further research into mixed metal catalysts and reaction mechanisms continues to push the boundaries of ethanol dehydration efficiency and scalability.

3.7. Proposed Dehydration Reaction Mechanism

Figure 9 illustrates the dehydration mechanism of ethanol to diethyl ether utilizing a Cr-Co/γ-Al_2O_3 catalyst. The figure likely depicts the catalytic pathway and intermediate species involved in the conversion of ethanol to diethyl ether, highlighting the role of the catalyst in facilitating this transformation. Overall, optimizing the reaction conditions and addressing factors affecting yield, such as condensation efficiency and minimizing competing reactions, will be essential for enhancing diethyl ether production in future studies.

Diethyl ether (DEE) formation can proceed via two distinct pathways: the dissociative pathway and the associative pathway. In the dissociative pathway, the process begins with the adsorption of one ethanol molecule onto the catalyst surface. This leads to the elimination of water, resulting in the formation of adsorbed ethyl groups. Subsequently, these ethyl groups react with a second ethanol molecule, ultimately yielding diethyl ether. Conversely, the associative

Table 2. A comparison of several studies on ethanol dehydration

Catalyst	Reactor	Reaction temperature (℃)	Ethanol conversion (%)	DEE Yield (%)	Reference
HZSM-5	Fixed bed	300	95.1	0.5	[13]
NiAPSO-34	reactor	350	93.9	1	
SAPO-34		350	91.2	4.9	
γ-Al_2O_3		450	865.6	6.9	
Al_2O_3	Fixed bed	200-400	14.1-84.5	28 (250 ℃)	[26]
5P/Al_2O_3	microreactor	200-400	9.1-86.1	35 (300 ℃)	
12P/Al_2O_3		200-400	8.1-72.9	31 (300 ℃)	
14P/Al_2O_3		200-400	4.6-35.5	11 (400 ℃)	
20P/Al_2O_3		200-400	0-17.2	9 (400 ℃)	
Bo/Al_2O_3	Fixed bed reactor	300	15-100	57	[27]
HBZ	Fixed-bed	250	66	35	[28]
Ru-HBZ	continuous flow	250	73	47	
Pt-HBZ	microreactor	250	70	45	
ZrO_2	Tubular flow	250-350	0-45	0-3	[29]
TiO_2	reactor	200-350	0-80	1-47	
WO_3/ZrO_2		150-250	1-54	1-42	
WO_3/TiO_2 (H)		150-250	12-89	10-68	
2%PHZSM-5	Fixed bed	200-240	69-96	23-66	[30]
0.5% LaHZSM-5	reactor	200	86	29	
H-ZSM-5	Fixed bed	300	90	14	[14]
20HP-ZSM-5	continuous flow stainless steel microreactor	250-450	25-100	0-24	

pathway involves the co-adsorption of two ethanol molecules. These co-adsorbed ethanol molecules react directly with each other to form diethyl ether.

The dehydration of alcohol primarily occurs at Brønsted acid sites [16,31], which facilitate the necessary proton transfer during the reaction. In contrast, Lewis acid sites play a minimal role in this particular reaction mechanism [32,33]. The presence of Brønsted acid sites enhances the catalyst's ability to promote the dehydration reaction, leading to more efficient diethyl ether production. Understanding the mechanisms behind diethyl ether formation is crucial for optimizing catalyst design and reaction conditions, which can ultimately improve yields and selectivity for the desired product.

3. Conclusions

The Cr-Co/γ-Al_2O_3 catalysts, prepared via dry impregnation with varying metal ratios, demonstrate significant potential for diethyl ether (DEE) production through ethanol dehydration. The study reveals that the impregnation of chromium and cobalt leads to a reduction in the total surface area of γ-Al_2O_3, primarily due to the clogging of alumina pores by the metal species. Among the catalysts evaluated, the Cr-Co 21 catalyst exhibited the highest performance, achieving an ethanol conversion of 93.12 % and a DEE yield of 1.32 % at a reaction temperature of 200 °C with a metal loading ratio of 2:1. The DEE yield order for the 10 wt.% Cr-Co/γ-Al_2O_3 catalyst in a fixed-bed reactor at 200 °C was Cr-Co 21 > Cr-Co 22 > Cr-Co 11. These findings underscore the effectiveness of the Cr-Co/γ-Al_2O_3 catalysts, particularly the Cr-Co 21 variant, in facilitating ethanol dehydration to diethyl ether, highlighting the crucial role of metal loading ratios and reaction conditions in optimizing catalyst performance for industrial applications. Future research should focus on optimizing the Cr-Co catalyst composition, particularly exploring different metal loading ratios and impregnation techniques to further enhance the surface area and catalytic efficiency. Additionally, the development of novel support materials with higher thermal stability and resistance to pore blockage could help mitigate surface area loss, thereby improving catalyst longevity and performance. Investigating the kinetics of the reaction and exploring alternative reactor designs, such as fluidized-bed or microchannel reactors, may also provide valuable insights into scaling the process for industrial use.

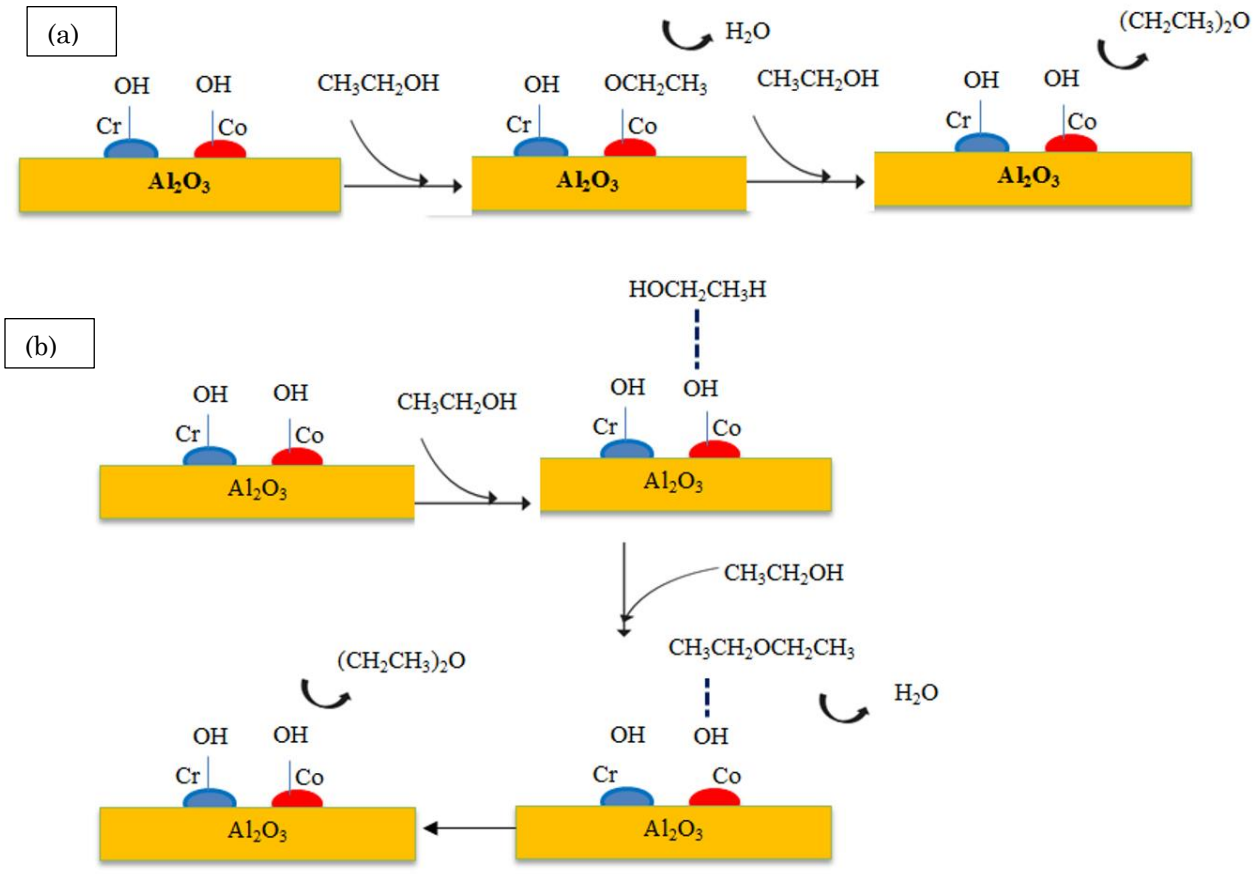

Figure 9. Ethanol dehydration to DEE by (a) the dissociative pathway and (b) the associative pathway at Cr-Co/γ-Al_2O_3 catalyst

Acknowledgment

The author would like to express his gratitude to the Government of Indonesia, in this case the the Ministry of Religion Affair, Republic of Indonesia which has provided scholarship funds for the Doctoral Program and research funds.

CRedit Author Statement

Author Contributions: A. Roesyadi: Conceptualization, Methodology, Resources, Project Administration; Supervision; M. Mahfud: Conceptualization, Formal Analysis, Review and Editing Writting, F Kurniawansyah: Preparation, Validation, Writing; I.A Muna: Investigation, Resources, Data Curation Draft writing. All authors have read and agreed to the published version of the manuscript.

References

[1] Ibrahim, A. (2016). Investigating the effect of using diethyl ether as a fuel additive on diesel engine performance and combustion. *Applied Thermal Engineering*, 107, 853–862. DOI: 10.1016/j.applthermaleng.2016.07.061.

[2] Varışlı, D. (2007). Kinetic studies for dimethyl ether and diethyl ether production. Doktora Tezi

[3] Ullmann, U. (1987). *Ullmann's Encyclopedia of Industrial Chemistry*, 5th ed. Weinhem Federal Republic of Germany: VCH Verlagsgesellschaft.

[4] DeWilde, J.F., Chiang, H., Hickman, D.A., Ho, C.R., Bhan, A. (2013). Kinetics and mechanism of ethanol dehydration on γ-Al 2O3: The critical role of dimer inhibition. *ACS Catalysis*, 3(4), 798–807. DOI: 10.1021/cs400051k.

[5] Han, Y., Lu, C., Xu, D., Zhang, Y., Hu, Y., Huang, H. (2011). Molybdenum oxide modified HZSM-5 catalyst: Surface acidity and catalytic performance for the dehydration of aqueous ethanol. *Applied Catalysis A: General*, 396(1–2), 8–13. DOI: 10.1016/j.apcata.2010.12.040.

[6] Poole Jr, C.P., Mac Iver, D.S. (1957). The Physical Properties of Chromia-Alumina Catalysts. *Advances in Catalysis*, 9(C), 155–162. DOI: 10.1016/S0360-0564(08)60164-9.

[7] Srinivasan, P.D., Khivantsev, K., Tengco, J.M.M., Zhu, H., Bravo-Suárez, J.J. (2019). Enhanced ethanol dehydration on γ-Al2O3 supported cobalt catalyst. *Journal of Catalysis*, 373, 276–296. DOI: 10.1016/j.jcat.2019.03.024.

[8] Phung, T.K., Lagazzo, A., Rivero Crespo, M.Á., Sánchez Escribano, V., Busca, G. (2014). A study of commercial transition aluminas and of their catalytic activity in the dehydration of ethanol. *Journal of Catalysis*, 311, 102–113. DOI: 10.1016/j.jcat.2013.11.010.

[9] Rodríguez-González, L., Hermes, F., Bertmer, M., Rodríguez-Castellón, E., Jiménez-López, A., Simon, U. (2007). The acid properties of H-ZSM-5 as studied by NH3-TPD and 27Al-MAS-NMR spectroscopy. *Applied Catalysis A: General*, 328(2), 174–182. DOI: 10.1016/j.apcata.2007.06.003.

[10] Sousa, Z.S.B., Veloso, C.O., Henriques, C.A., Teixeira da Silva, V. (2016). Ethanol conversion into olefins and aromatics over HZSM-5 zeolite: Influence of reaction conditions and surface reaction studies. *Journal of Molecular Catalysis A: Chemical*, 422, 266–274. DOI: 10.1016/j.molcata.2016.03.005.

[11] Chiang, H., Bhan, A. (2010). Catalytic consequences of hydroxyl group location on the rate and mechanism of parallel dehydration reactions of ethanol over acidic zeolites. *Journal of Catalysis*, 271(2), 251–261. DOI: 10.1016/j.jcat.2010.01.021.

[12] Takahara, I., Saito, M., Inaba, M., Murata, K. (2005). Dehydration of ethanol into ethylene over solid acid catalysts. *Catalysis Letters*, 105(3–4), 249–252. DOI: 10.1007/s10562-005-8698-1.

[13] Zhang, X., Wang, R., Yang, X., Zhang, F. (2008). Comparison of four catalysts in the catalytic dehydration of ethanol to ethylene. *Microporous and Mesoporous Materials*, 116(1–3), 210–215. DOI: 10.1016/j.micromeso.2008.04.004.

[14] Ramesh, K., Hui, L.M., Han, Y.F., Borgna, A. (2009). Structure and reactivity of phosphorous modified H-ZSM-5 catalysts for ethanol dehydration. *Catalysis Communications*, 10(5), 567–571. DOI: 10.1016/j.catcom.2008.10.034.

[15] Sheng, Q., Ling, K., Li, Z., Zhao, L. (2013). Effect of steam treatment on catalytic performance of HZSM-5 catalyst for ethanol dehydration to ethylene. *Fuel Processing Technology*, 110, 73–78. DOI: 10.1016/j.fuproc.2012.11.004.

[16] Xin, H., Li, X., Fang, Y., Yi, X., Hu, W., Chu, Y., Zhang, F., Zheng, A., Zhang, H., Li, X. (2014). Catalytic dehydration of ethanol over post-treated ZSM-5 zeolites. *Journal of Catalysis*, 312, 204–215. DOI: 10.1016/j.jcat.2014.02.003.

[17] Jingfa, D., Guirong, Z., Shuzhong, D., Haishui, P., Huaiming, W. (1988). Acidic properties of ZSM-5 zeolite and conversion of ethanol to diethyl ether. *Applied Catalysis*, 41(C), 13–22. DOI: 10.1016/S0166-9834(00)80378-4.

[18] Alharbi, W., Brown, E., Kozhevnikova, E.F., Kozhevnikov, I.V. (2014). Dehydration of ethanol over heteropoly acid catalysts in the gas phase. *Journal of Catalysis*, 319, 174–181. DOI: 10.1016/j.jcat.2014.09.003.

[19] Kamsuwan, T., Jongsomjit, B. (2016). A comparative study of different al-based solid acid catalysts for catalytic dehydration of ethanol. *Engineering Journal*, 20(3), 63–75. DOI: 10.4186/ej.2016.20.3.63.

[20] Tresatayawed, A., Glinrun, P., Jongsomjit, B. (2019). Ethanol Dehydration over WO3/TiO2 Catalysts Using Titania Derived from Sol-Gel and Solvothermal Methods. *International Journal of Chemical Engineering*, 2019 DOI: 10.1155/2019/4936292.

[21] Chen, G., Li, S., Jiao, F., Yuan, Q. (2007). Catalytic dehydration of bioethanol to ethylene over TiO2/γ-Al2O3 catalysts in microchannel reactors. *Catalysis Today*, 125(1–2), 111–119. DOI: 10.1016/j.cattod.2007.01.071.

[22] de Oliveira, T.K.R., Rosset, M., Perez-Lopez, O.W. (2018). Ethanol dehydration to diethyl ether over Cu-Fe/ZSM-5 catalysts. *Catalysis Communications*, 104, 32–36. DOI: 10.1016/j.catcom.2017.10.013.

[23] Da Ros, S., Jones, M.D., Mattia, D., Schwaab, M., Noronha, F.B., Pinto, J.C. (2017). Modelling the effects of reaction temperature and flow rate on the conversion of ethanol to 1,3-butadiene. *Applied Catalysis A: General*, 530, 37–47. DOI: 10.1016/j.apcata.2016.11.008.

[24] Chen, Y., Wu, Y., Tao, L., Dai, B., Yang, M., Chen, Z., Zhu, X. (2010). Dehydration reaction of bio-ethanol to ethylene over modified SAPO catalysts. *Journal of Industrial and Engineering Chemistry*, 16(5), 717–722. DOI: 10.1016/j.jiec.2010.07.013.

[25] Peng, B., Dou, H., Shi, H., Ember, E.E., Lercher, J.A. (2018). Overcoming Thermodynamic Limitations in Dimethyl Carbonate Synthesis from Methanol and CO2. *Catalysis Letters*, 148(7), 1914–1919. DOI: 10.1007/s10562-018-2402-8.

[26] Limlamthong, M., Chitpong, N., Jongsomjit, B. (2019). Influence of phosphoric acid modification on catalytic properties of Al2O3 catalysts for dehydration of ethanol to diethyl ether. Bull. Chem. React. Eng. Catal. 14:1–8.

[27] Chaichana, E., Boonsinvarothai, N., Chitpong, N., Jongsomjit, B. (2019). Catalytic dehydration of ethanol to ethylene and diethyl ether over alumina catalysts containing different phases with boron modification. *Journal of Porous Materials*, 26(2), 599–610. DOI: 10.1007/s10934-018-0663-7.

[28] Kamsuwan, T., Praserthdam, P., Jongsomjit, B. (2017). Diethyl ether production during catalytic dehydration of ethanol over ru- and pt- modified h-beta zeolite catalysts. *Journal of Oleo Science*, 66(2), 199–207. DOI: 10.5650/jos.ess16108.

[29] Phung, T.K., Hernández, L.P., Busca, G. (2015). Conversion of Ethanol over transition metal oxide catalysts: Effect of tungsta addition on catalytic behaviour of titania and zirconia. *Applied Catalysis A: General*, 489, 180–187. DOI: 10.1016/j.apcata.2014.10.025.

[30] Zhan, N., Hu, Y., Li, H., Yu, D., Han, Y., Huang, H. (2010). Lanthanum-phosphorous modified HZSM-5 catalysts in dehydration of ethanol to ethylene: A comparative analysis. *Catalysis Communications*, 11(7), 633–637. DOI: 10.1016/j.catcom.2010.01.011.

[31] Hong, E., Sim, H.I., Shin, C.H. (2016). The effect of Brønsted acidity of WO3/ZrO2 catalysts in dehydration reactions of C3 and C4 alcohols. *Chemical Engineering Journal*, 292, 156–162. DOI: 10.1016/j.cej.2016.01.042.

[32] Moser, W.R., Thompson, R.W., Chiang, C.C., Tong, H. (1989). Silicon-rich H-ZSM-5 catalyzed conversion of aqueous ethanol to ethylene. *Journal of Catalysis*, 117(1), 19–32. DOI: 10.1016/0021-9517(89)90217-0.

[33] Nash, C.P., Ramanathan, A., Ruddy, D.A., Behl, M., Gjersing, E., Griffin, M., Zhu, H., Subramaniam, B., Schaidle, J.A., Hensley, J.E. (2016). Mixed alcohol dehydration over Brønsted and Lewis acidic catalysts. *Applied Catalysis A: General*, 510, 110–124. DOI: 10.1016/j.apcata.2015.11.019.