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Original Research Article

Modification of HZSM-5 with Phosphotungstate, Silver, and Cobalt to Enhance Catalytic Reaction of Bioethanol to Bioethylene

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Abstract

Developing an optimal catalyst formulation is a critical challenge in expanding sustainable ethylene production and utilization as a chemical intermediate product. Metal oxide impregnation (silver nitrate ($AgNO_3$), cobalt nitrate ($Co(NO_3)_2$), and phosphotungstic acid ($H_3PW_{12}O_{40}$)) was used to enhance the catalytic performance of HZSM-5 by increasing active sites and acidity. The preparation of the catalyst was performed by the impregnation of various metals and amounts of loading particles inside the pores of HZSM-5. The particles were impregnated by incipient wetness impregnation and followed by calcination to obtain Ag/HZSM-5, Co/HZSM-5, and W/HZSM-5 catalysts. Characterization techniques, including N_2 adsorption-desorption, SEM, and XRD, were used to analyze the catalyst properties. Catalytic performance was evaluated in a packed-bed reactor under varying reaction conditions at WHSV 1.8 h^{-1}. The aim of this research is to identify optimal catalyst formulations that exhibit superior activity in both conversion and selectivity towards ethylene production. Modified HZSM-5 catalysts incorporating Ag, Co, and W exhibited enhanced catalytic performance for bioethanol dehydration to bioethylene, attributed to optimized acidic sites, pore structure, and metal synergy. The 1%W/HZSM-5 catalyst demonstrated superior ethylene conversion (98.2%) and selectivity (99.88%) at 300 °C. Increasing tungsten loading up to 2% impacted the conversion of bioethanol.

Keywords: Alcohol Dehydration; HZSM-5; Metal Oxide Modification; Bio-based Hydrocarbon

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1. Introduction

Ethylene is an important chemical commodity in the petrochemical industry. The high demand for ethylene is driven by its use in producing numerous products, including polyethylene, ethylene glycol, ethylene oxide, and polyvinyl chloride [1]. The global consumption of ethylene has been steadily rising, driven by increasing industrialization and population growth. In 2016, global ethylene demand surpassed 150 million tons [2], with projections indicating a sustained growth rate of approximately 3% per year [3].

Traditionally, ethylene has been produced by the steam cracking of hydrocarbons, a process that is energy-intensive and contributes significantly to greenhouse gas emissions [4]. Hydrocarbon compounds with a large number of carbon atoms can be cracked at high temperature into smaller hydrocarbon compounds [5]. About 99% of the global ethylene is synthesized by this method [6]. However, steam cracking operates at 800 – 1200 °C and accounts for over 95% of global ethylene

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production, resulting in a large carbon footprint and significant CO_2emissions [7]. As the demand for ethylene continues to rise, coupled with the decreasing supply of fossil fuels, there is an urgent need to develop more sustainable alternatives.

Several methods have garnered global attention, with biomass emerging as one of the most promising renewable energy resources. Catalytic dehydration of bioethanol offers a promising green alternative to conventional ethylene production. This route enables renewable feedstocks to be used under milder conditions while achieving high ethylene selectivity [8]. This process offers several advantages, including lower reaction temperatures, higher ethylene yields, and the utilization of a renewable feedstock [9]. Moreover, commercial-scale bioethanol-to-ethylene plants, such as those operated by Braskem and Solvay in Brazil, demonstrate the economic and environmental viability of this approach [10]. Additionally, the catalytic dehydration of bioethanol can contribute to reducing greenhouse gas emissions and promoting a more sustainable energy future.

The development of an efficient catalyst is crucial for optimizing the bioethanol dehydration process and achieving commercial profitability. Zeolite Socony Mobile-5 (ZSM-5), a zeolite with strong acidic properties and high selectivity for ethylene, has been widely studied as a catalyst for dehydration reaction [11]. Nanoscale and hierarchical ZSM-5 catalysts have shown superior resistance to coke formation and higher long-term stability [12,13]. However, to enhance the catalytic performance and reduce energy consumption, modifications such as metal oxide impregnation are required.

Metal impregnation and framework modification adjust the ratio of Brønsted and Lewis acid sites, improving ethanol conversion at lower temperatures [14,15]. By increasing the number of active sites and improving catalyst acidity, these modifications aim to lower the reaction temperature while maintaining high ethylene yields [16]. This performance is strongly correlated to the number and strength of acid sites, which can be tuned by rare-earth or transition-metal doping [17]. Similarly, controlling surface acidity, such as through phosphate or metal oxide modification, enhances selectivity and catalyst stability [18]. Recent work also indicates that catalysts like Ni/Sr-ZSM-5 maintain high yield even in aqueous ethanol feed, highlighting their suitability for bioethanol-derived feeds [19]. In particular, phosphotungstic acid modification of HZSM-5 optimizes acidic distribution and pore structure, improving stability and promoting ethylene selectivity [20].

Several studies have reported the catalytic performance of different ZSM-5-based catalysts for ethanol dehydration. γ-Al_2O_3 catalysts can achieve very high ethanol conversion and ethylene selectivity (up to 99.7% and 98.6%, respectively), but typically require high reaction temperatures around 440 °C [29], while performance drops significantly at lower temperatures [30]. In contrast, nanosized HZSM-5 has demonstrated high activity at lower temperatures (200–300 °C), achieving ethanol conversion of 98.6% and ethylene selectivity of 99.2% at 240 °C due to its thermal stability and favorable microporous structure [31]. Various catalyst modifications have also been explored to improve stability and selectivity. Lanthanum–phosphorus-modified HZSM-5 achieved nearly complete ethanol conversion with ethylene selectivity of 99.9% at 240 °C [32], while phosphorus-modified ZSM-5 reached ethylene yields above 94% under similar conditions [4]. Moreover, Ce-impregnated HZSM-5 showed enhanced stability, maintaining ethylene selectivity of approximately 76% over 140 h time-on-stream compared with rapid deactivation of the unmodified catalyst [33]. Despite these advances, many studies still focus on single modifiers, operate under different experimental conditions, or lack systematic comparisons of multiple co-catalysts under identical operating parameters, making it difficult to directly evaluate the relative effectiveness of different metal or heteropolyacid impregnations.

This study focuses on modifying HZSM-5 catalysts through metal oxide impregnation to enhance their catalytic performance for bioethanol dehydration. The experiments include catalyst preparation, characterization, and catalytic performance evaluation under various reaction conditions. The goal was to identify an optimal catalyst with superior catalytic activity and selectivity. The findings of this research could have significant implications for the petrochemical industry, potentially reducing its reliance on fossil fuels and promoting a transition to a more circular economy.

2. Materials and Methods

2.1 Materials

The materials used to prepare the modified catalyst are ZSM-5 (SiO_2/Al_2O_3 molar ratio = 38, surface area ≥ 250 m^2/g) from ACS Material LLC (Pasadena, USA). The co-catalyst, including silver nitrate ($AgNO_3$), cobalt nitrate hexahydrate ($Co(NO_3)_2.6H_2O$), and phosphotungstic acid ($H_3PW_{12}O_{40}$) from Merck Chemical Co. (Jakarta, Indonesia), was of analytical grade and used as received. The other materials used for the catalytic test were ethanol (99%) from Merck Chemical Co (Jakarta, Indonesia), nitrogen (99.5%) as an inert gas, and deionized water obtained from Polymer Technology Laboratory UGM.

2.2. Methods

2.2.1. Modification for incorporation of metal

The unmodified HZSM-5 was grounded to obtain particles under 2 mm in length. The material was then filtered and dried before being impregnated with metals. The modified HZSM-5 catalysts using metals (Ag, Co, and W) were synthesized by treating the pure HZSM-5 with metal solution in a two-step method of impregnation of metal and followed by calcination at various temperatures according to the kind of metal. The choice of Ag, Co, and W metals to modify HZSM-5 is based on their specific properties that can enhance the catalytic performance of the zeolite in terms of selectivity, activity, and stability.

The HZSM-5 was impregnated using the incipient wetness method, which involves adding a liquid solution of the impregnant to the zeolite in a vacuum condition until the first signs of wetting are observed, according to references [21, 22]. The solutions were made of $Ag(NO_3)_2$, $Co(NO_3)_2 \cdot 6H_2O$, or $H_3PW_{12}O_{40}$ dissolved in deionized water with metal loading of 1% (w.t), respectively. This method was chosen to obtain a uniform distribution of the active component. Subsequently, to promote the formation of crystalline metal oxides, the materials were dried for 24 h at 70 ℃ in an oven and activated by calcination at various temperature and time; 600 ℃ for 4 h (Ag), 600 ℃ for 4 h (Co), and 500 ℃ for 5 h (W) in a horizontal furnace (OTF 1200X, MTI Corp.) with heating rate of 3 ℃/min under nitrogen atmosphere. The final products were labelled Ag/HZSM-5, Co/HZSM-5, and W/HZSM-5. The steps were repeated for 0.5% and 2% loading rates of HPW metal.

2.2.2. Characterization of materials

Pore structure characterization was evaluated by N_2 adsorption–desorption analysis (Nova 2000 Quantachrome, USA). The specific surface area (SSA) was calculated from N_2 sorption data using the Brunauer-Emmett-Teller (BET) method. The pore size distributions and fraction of micropore volume were evaluated using the Quenched Solid Density Functional Theory (QSDFT) model and t-plot method, respectively. Morphology and elemental composition of materials were examined by Scanning Electron Microscope (JEOL JSM-6510 LA, JEOL Ltd., Japan), coupled with energy-dispersive X-Ray (EDX) mapping analyzer. On the other hand, the crystal of metal oxide was analyzed by X-ray diffraction. XRD patterns were recorded using an X-ray diffractometer (Bruker D2 Phaser 2^{nd} Gen, Germany) with Cu radiation by using 0.5 gram of the catalyst powder and instrumental settings at 40 mA and 40 kV. The scanning range was from 2° to 90°.

2.2.3. Catalytic performance

The dehydration reaction was performed in a packed-bed reactor. Catalysts were added in a tubular quartz tube (diameter 1 cm; length 30 cm) isolated by glass wool. Subsequently, the tubular reactor was placed in an electrically heated furnace. The catalyst bed was 5 cm in height to keep gas flow rates within bounds. The equipment was flushed by nitrogen purge gas at 50 mL/min for 30 minutes through the system to evacuate dissolved oxygen in the reactor. The temperature of the reactor was controlled at 220-260 ℃ using a temperature controller through a type of thermocouple (Lutron; TM-936, Taiwan). Ethanol was heated in a boiler to form steam at a constant temperature of 63 ℃ and then carried into the reactor under a nitrogen gas flow rate of 50 mL/min, bubbled by a sparger. The WHSV of ethanol was set at 1.8 h^{-1}. The dissolved gas outlet reactor was trapped in deionized water and then was analyzed using a Gas Chromatography Flame Ionization Detector (GC−FID; GC14B, Shimadzu, Japan) which was performed using Free Fatty Acid Phase (FFAP) fused-silica capillary column to determine the leftover unreacted ethanol. Ethylene, as a non-dissolved gas product, was withdrawn at a time interval of 2 h, and it was analyzed using a GC−TCD (GC8A, Shimadzu, Japan). The product gas sample was injected into the Gas Chromatography at a value of 0.5 mL. The column temperature was at 70 ℃ with a TCD temperature of 100 ℃ with 70 mA current.

3. Results and Discussion

3.1. Material Characteristics

3.1.1. Morphology and elemental analysis

SEM was used to evaluate the surface and structural characteristics. Figure 1a – 1d are images of SEM analysis showing the surface morphology of 1%Ag/HZSM-5 (a), 1%Co/HZSM-5 (b), 1%W/HZSM-5 (c), and unmodified HZSM-5 (d) catalyst. The surface of the four catalysts is covered with white crystals. All of the modified materials with 1% metal loading had morphological characteristics similar to the unmodified HZSM-5, indicating that the morphological integrity of the catalyst was not affected by desilication.

Based on the SEM images of 1%Ag/HZSM-5, 1%Co/HZSM-5, 1%W/HZSM-5, and unmodified HZSM-5, there were no significant changes in morphological integrity. The surface morphology of all modified catalysts appears similar to that of the unmodified HZSM-5. It suggests that the metal species are likely incorporated into the zeolite framework or present as very small particles and seem to be well-dispersed throughout the material, which is indicative of a homogeneous distribution of the metal species.

The crystallite size of the zeolite appears relatively uniform across all samples. The crystallites are consistent with the zeolite's structure. Overall, the desilication process did not significantly alter the overall structure of the zeolite.

Similar to Figure 1, metal modifications with varying loading amounts also have the same characteristics as the unmodified HZSM-5, as depicted in Figure 2. This indicates that the morphological integrity of the catalyst and that there were no defects during metal loading. The SEM analysis indicates that the modification process did not significantly alter the fundamental structure of the HZSM-5 zeolite. To see the dispersion of elemental content, SEM-EDX was performed in 1%W/HZSM-5 as a representative as shown in Figure 3. It can be seen that elementals of W and P in phosphotungstic acid are homogeneously dispersed. It is an indication that the preparation of material was successful. However, further characterizations are required, e.g. TEM analysis to elucidate the precise location and dispersion of the metal species within the zeolite framework.

3.1.2. Nitrogen adsorption and desorption isotherm

The nitrogen adsorption and desorption of all materials were characterized, as shown in Figure 4. The upper line represents the adsorption isotherm, which shows the amount of gas adsorbed by the catalyst as the relative pressure increases. The lower line represents the desorption isotherm, which shows the amount of gas desorbed from the catalyst as the relative pressure decreases. The isotherms of all characterized materials correspond to a combination of Type I and Type IV isotherms. Type I isotherms indicate the micropores in materials as defined by IUPAC nomenclature [23], both unmodified HZSM-5 and those modified with Ag, Co, and W. Based on the hysteresis type and isotherm at P/Po > 0.1, all materials also correspond to Type IV isotherm and hysteresis. However, adsorption of nitrogen >P/Po 0.1 is higher than the lower one, which indicates that a dominant proportion of mesopores are present. The shape of the H4 hysteresis loop suggests a narrow pore size distribution with ink-bottle-shaped pores [24]. It can be seen that unmodified material can absorb slightly more nitrogen than modified material, especially at low pressure. This indicates that metal impregnation of zeolite can reduce the pore volume of material. The decrease in pore volume

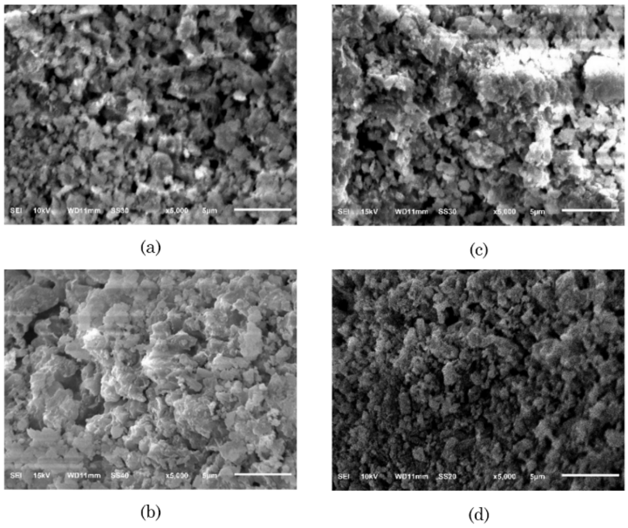


Figure 2. SEM images of (a) 0.5%W/HZSM-5, (b) 1%W/HZSM-5, (c) 2%W/HZSM-5 and (d) HZSM-5.

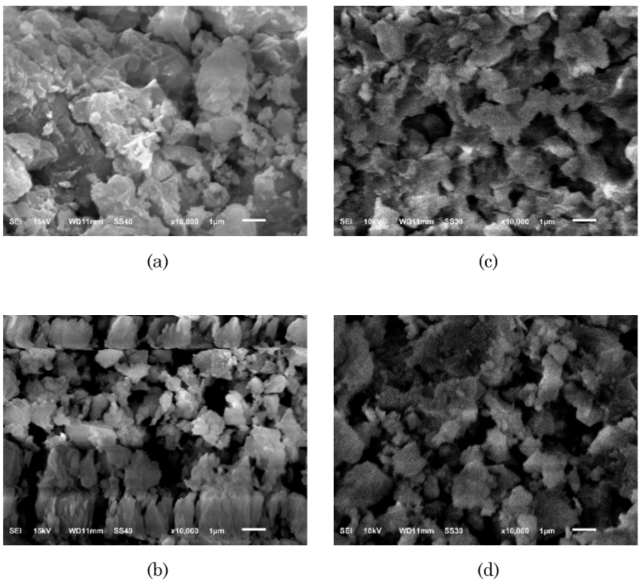


Figure 1. SEM images of (a) 1%Ag/HZSM-5, (b) 1%Co/HZSM-5, (c) 1%W/HZSM-5, and (d) HZSM-5.

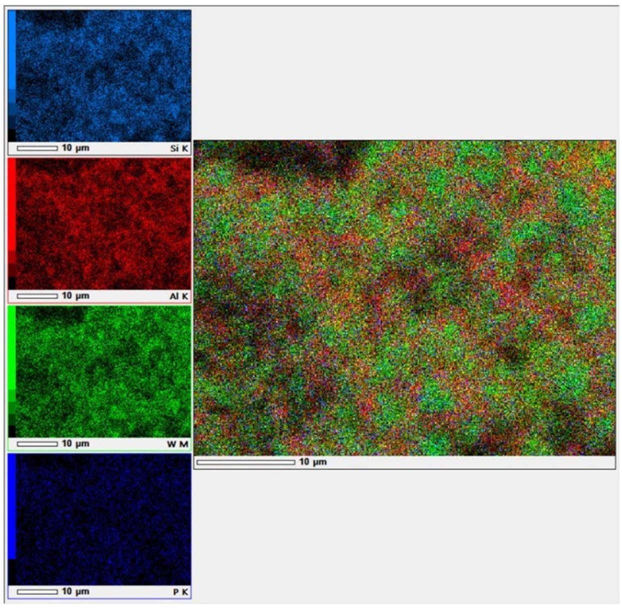


Figure 3. EDX mapping of 1%W/HZSM-5 (blue = Si; red = Al; green = W; dark blue = P).

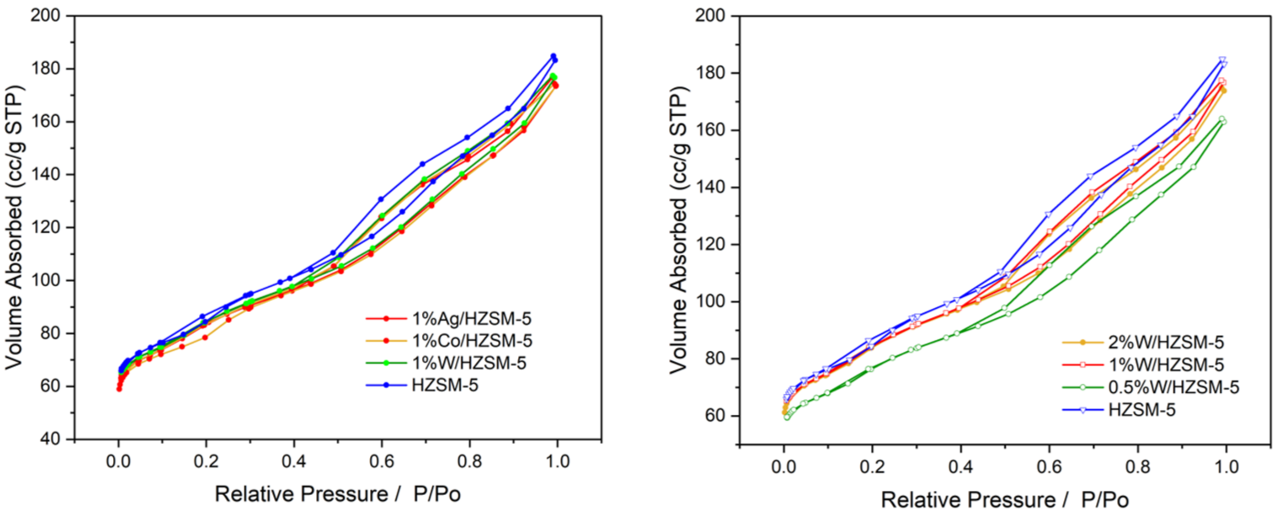
after metal impregnation can be attributed to partial pore blocking and narrowing of the zeolite channels by deposited metal or metal oxide species. During impregnation and calcination, the metal can penetrate into the micropores and subsequently form oxide clusters that occupy pore space or block pore entrances, thereby reducing the accessible pore volume measured by nitrogen adsorption, while the zeolite framework structure remains preserved.

3.1.3. Pore size distribution

In the pore size distribution graph, the relative number of pores with a given diameter for each material being characterized is shown in Figure 5. A larger specific pore volume shows a larger number of pores with a specific diameter. All materials show a sharp peak at a very small pore width (around 1-5 nm), which indicates the dominance of micropores. However, the impregnation of metal into zeolite can reduce the number of micropores. The reduction of micropores after metal impregnation is attributed to partial pore blocking by metal species, as indicated by the decrease in micropore volume and the reduced intensity of the micropore peak (1–5 nm) in the pore size distribution compared to the parent HZSM-5. Similar effects have been widely reported for metal-modified HZSM-5 catalysts [31,32].

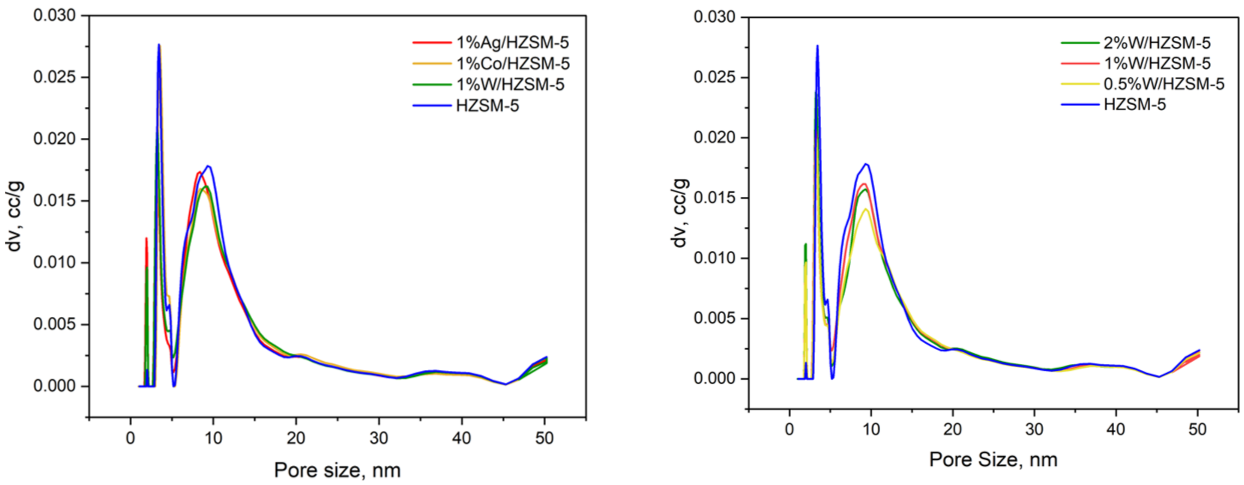
3.1.4. Surface area material characteristics

The pore structure properties of materials are shown in Table 1. The impregnation of various kinds of metal and various amounts of loading reduces both the specific surface area and micropore percentage due to the introduced particles entering and blocking micropores in the



(a) (b)

Figure 4. Nitrogen adsorption-desorption isotherms of (a) modified HZSM-5 at various kinds of metals and (b) modified HZSM-5 at various amounts of loading.



(a) (b)

Figure 5. Pore size diameter of (a) modified HZSM-5 at various kinds of metal and (b) modified HZSM-5 at various amounts of loading.

zeolite. The same phenomenon is seen for the total pore volume of each material.

3.1.5. X-Ray diffraction spectrum

This XRD analysis reveals a crystalline structure supporting the catalytic function [25]. XRD patterns of materials are shown in Figure 6. The materials have a fairly high agreement between the main peaks and the Joint Committee on Powder Diffraction Standards (JCPDS) literature [26]. Figure 6 shows that the material has two main peaks at 2θ = 7-9° and 22-25°, which match the representation of the crystal phase of zeolite. All materials had almost identical peaks, indicate that the basic structure of HZSM-5 zeolite does not change significantly after being modified due to the small amount of metal particles. Diffraction peaks associated with Ag, Co, W, or Ni species were not detected in the XRD patterns of the modified catalysts. This absence can be attributed to the low metal loading (≤1 wt%) and the high dispersion of metal species on the zeolite surface, which are below the detection limit of conventional XRD analysis. Highly dispersed metal or metal oxide species, particularly when present as nanosized clusters or amorphous phases, often do not generate detectable diffraction signals. Similar observations have been widely reported for metal-loaded zeolite catalysts with low metal content [34]. Therefore, the XRD results suggest that metal impregnation does not disrupt the zeolite framework and that the active metal species are

Table 1. Summarized pore characteristics of modified HZSM-5 and unmodified HZSM-5.

Sample	Specific Surface Area ($m^2.g^{-1}$)	Average Pore Diameter (nm)	Micropore Volume Fraction (%)	Total Pore Volume ($cm^3.g^{-1}$)
1% Ag/HZSM-5	291.13	3.68	90.54	0.26
1% Co/HZSM-5	284.94	3.76	91.09	0.26
1% W/HZSM-5	294.13	3.71	90.78	0.27
0.5% W/HZSM-5	294.72	3.62	90.76	0.26
2% W/HZSM-5	292.27	3.68	90.77	0.26
HZSM-5	303.13	3.73	91.72	0.28

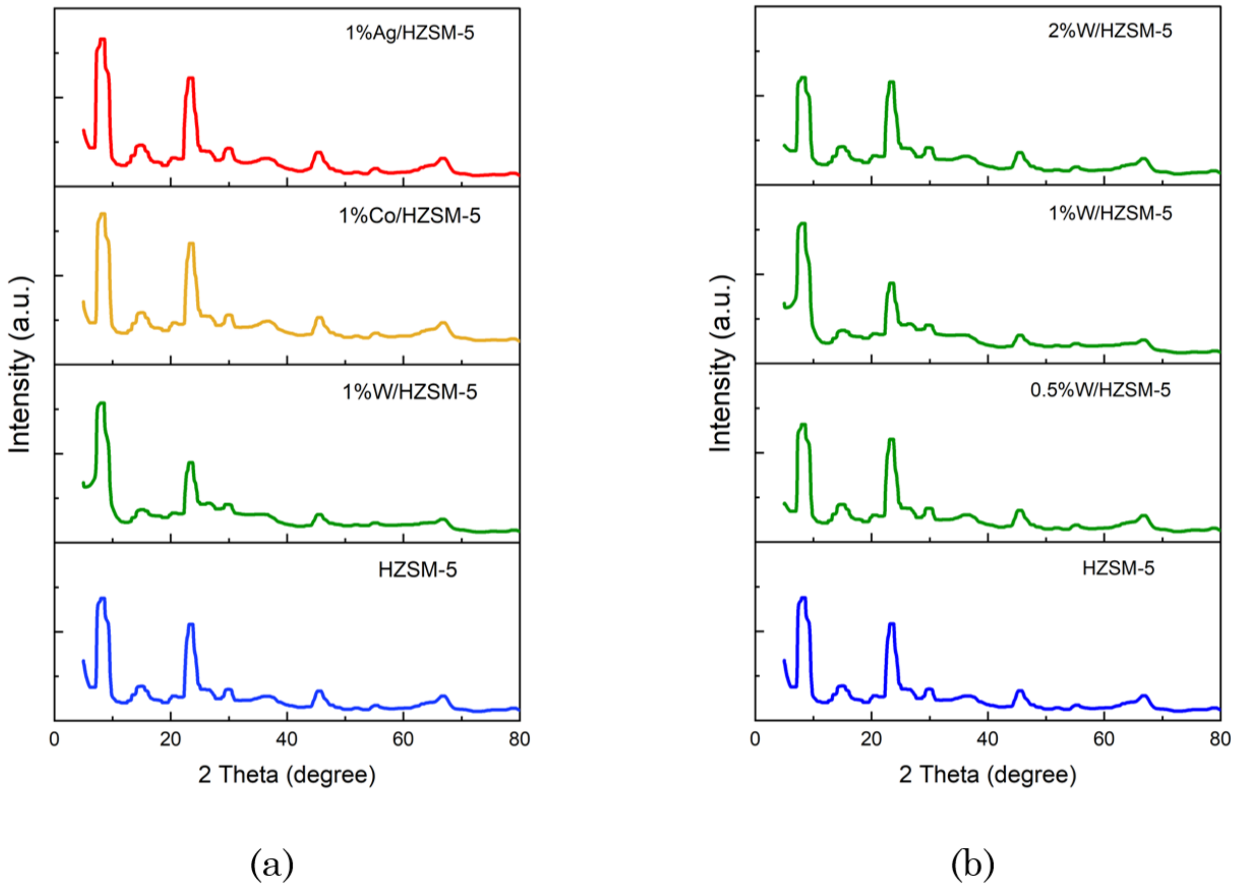


Figure 6. XRD spectra of (a) modified HZSM-5 at various metals, (b) modified HZSM-5 at various amounts of loading.

likely well dispersed on or within the HZSM-5 structure.

3.1.6. Point of Zero Charge (PZC) analysis

The surface acidity of the catalysts was evaluated using the Point of Zero Charge (PZC) method to qualitatively assess the acid–base properties of the modified HZSM-5 catalysts. The pH_{PZC} represents the pH value at which the net surface charge of a solid is zero. A lower pH_{PZC} indicates a more acidic surface, while a higher pH_{PZC} reflects a more basic character. Surface acidity plays a critical role in ethanol dehydration reactions, as it influences the adsorption strength of ethanol molecules, the formation of surface ethoxy intermediates, and the subsequent dehydration pathways toward ethylene. The pH_{PZC} values of the catalysts are summarized in Table 2, and the determination curves are shown in Figures 7.

The pure HZSM-5 exhibited a nearly neutral pH_{PZC} of 6.51, which is consistent with reported values for zeolitic materials ($pH_{PZC} \approx 6.8$) [reference]. After metal oxide impregnation, all modified catalysts showed a decrease in pH_{PZC}, indicating an increase in surface acidity. The Ag- and Co-modified catalysts exhibited moderate acidity with pH_{PZC} values of 6.21 and 6.08, respectively. In contrast, W-modified catalysts showed significantly lower pH_{PZC} values, with 0.5%W/HZSM-5, 1%W/HZSM-5, and 2%W/HZSM-5 presenting pH_{PZC} values of 4.39, 4.14, and 3.98, respectively.

The enhanced acidity induced by tungsten loading can be attributed to its higher electronegativity (Pauling electronegativity: W = 2.36, Co = 1.88, Ag = 1.93), which increases the polarity of W–O bonds and promotes electron withdrawal from the oxygen atoms in the zeolite framework. This effect increases the positive charge density on the catalyst surface and shifts the pH_{PZC} toward more acidic values. Furthermore, increasing tungsten loading progressively decreased the pH_{PZC}, confirming that higher metal content enhances surface acidity.

Although the PZC method does not provide quantitative information on acid site density and strength as obtained from TPD–NH_3 analysis, it offers reliable qualitative trends for comparing surface acidity among catalysts. These trends correlate well with the observed catalytic performance, particularly in terms of ethanol conversion and ethylene selectivity, indicating that surface acidity is a key factor governing catalytic activity.

3.2. Catalytic Performance

Table 3 depicts the performance of ethanol dehydration at WHSV 1.8 h^{-1}. All modified catalysts demonstrated high ethanol conversion, reaching nearly complete conversion (99.9%) at 300 ℃. The 1%W/HZSM-5 catalyst exhibited the highest conversion across all temperatures,

Table 2. pH_{PZC} values of HZSM-5-based materials.

Material	pH_{PZC}
1% Ag/HZSM-5	6.21
1% Co/HZSM-5	6.08
1% W/HZSM-5	4.14
0.5% W/HZSM-5	4.39
2% W/HZSM-5	3.98
HZSM-5	6.51

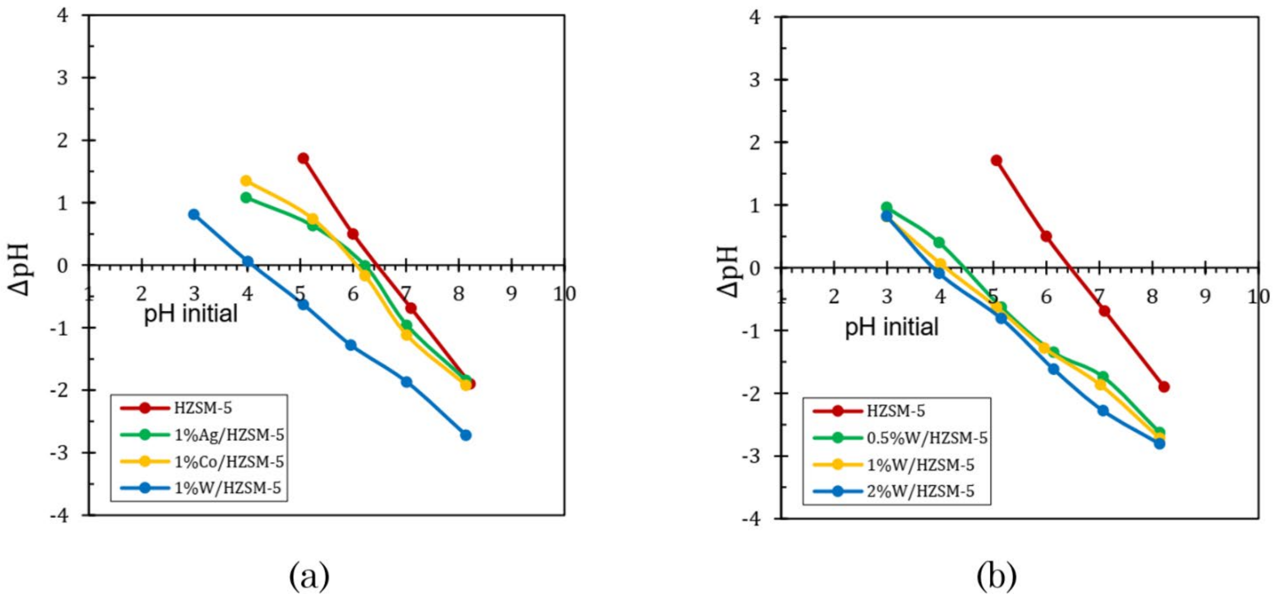


Figure 7. Plot for pH_{PZC} determination of (a) modified HZSM-5 at various metals, (b) modified HZSM-5 at various amounts of loading.

followed closely by 1%Co/HZSM-5 and 1%Ag/HZSM-5. The same phenomenon is seen at ethylene selectivity; the 1%W/HZSM-5 catalyst displayed the highest ethylene selectivity at all temperatures, reaching 71.13% at 300 °C. The 1%Co/HZSM-5 and 1%Ag/HZSM-5 catalysts also exhibited good ethylene selectivity, with values around 70% at 300 °C. The unmodified HZSM-5 showed the lowest ethylene conversion and selectivity, particularly at lower temperatures (260 °C and 280 °C).

The incorporation of metal species (Ag, Co, and W) into the HZSM-5 zeolite significantly enhanced both ethanol conversion and ethylene selectivity compared to the unmodified HZSM-5. This improvement is attributed to several factors that have been widely reported in the literature. Metal impregnation has been reported to modify the acidity of HZSM-5 by introducing additional Lewis acid sites, which favor ethanol dehydration reactions toward ethylene. In addition, metal incorporation may partially influence pore accessibility and diffusion pathways, potentially improving mass transfer within the zeolite framework. Similar effects of metal-modified HZSM-5 on ethanol dehydration activity and selectivity have been extensively reported in previous studies [27–29].

This observation aligns with previous findings that Lewis acid site generation via metal or oxide impregnation enhances alkene selectivity in modified HZSM-5 systems [27]. Furthermore, catalysts exhibiting an optimal balance between weak and moderate acidity, such as POC-derived SBA-15, display suppressed carbon deposition and enhanced ethylene selectivity [28]. Therefore, the high stability and selectivity of W/HZSM-5 can be attributed not only to its strong acid sites but also to its well-distributed weak-moderate acidity that prevents coke accumulation, consistent with previous observations for phosphotungstic-modified HZSM-5 [20].

Table 4 shows the effect of metal loading (W) on the catalytic performance. Increasing the tungsten loading from 0.5% to 1% led to a significant enhancement in both ethanol conversion and ethylene selectivity. However, further increasing the loading to 2% resulted in a slight decrease in ethylene selectivity, suggesting an optimal metal loading for maximizing ethylene production. Similar trends have been reported for other metal-modified zeolites, where excessive metal loading leads to site blocking and reduced accessibility of acid sites, consequently lowering selectivity [15]. While the metal modifications significantly improved the catalytic performance, temperature also played a crucial role. At lower temperatures (260 °C), the differences between the modified and unmodified catalysts were more pronounced, suggesting that the metal-induced acidity and improved mass transfer were particularly beneficial under these conditions. However, as the temperature increased to 300 °C, the differences between the catalysts became less significant, indicating that the intrinsic activity of the zeolite itself played a more dominant role at higher temperatures. This behavior is consistent with earlier studies showing that modified ZSM-5 catalysts maintain performance at high temperatures due to hierarchical pore structures and coke-resistant morphologies [13].

The optimum catalytic performance observed for the metal-modified HZSM-5 catalysts can be directly correlated with the physicochemical properties revealed by the characterization results. SEM analysis confirmed that metal impregnation did not alter the morphological integrity of the HZSM-5 framework, indicating good dispersion of metal species without structural collapse, which is essential for

Table 3. Performance of catalysts for the dehydration of ethanol over various metals.

Catalyst	Ethanol Conversion (%)			Ethylene Selectivity (%)		
	260 °C	280 °C	300 °C	260 °C	280 °C	300 °C
1%Ag/HZSM-5	82.16	97.52	99.96	44.73	66.01	66.86
1%Co/HZSM-5	88.16	97.92	99.91	80.81	97.28	99.87
1%W/HZSM-5	98.07	97.78	98.20	99.84	99.90	99.88
HZSM-5	69.57	69.60	93.82	30.86	55.76	92.24

Table 4. Performance of catalysts for the dehydration of ethanol at various amounts of loading.

Catalyst	Ethanol Conversion (%)			Ethylene Selectivity (%)		
	260 °C	280 °C	300 °C	260 °C	280 °C	300 °C
0.5%W/HZSM-5	63.58	75.85	76.04	95.37	93.77	94.63
1%W/HZSM-5	98.07	97.78	98.20	99.84	99.90	99.88
2%W/HZSM-5	97.19	97.91	98.08	96.82	98.02	98.10
HZSM-5	69.57	69.60	93.82	30.86	55.76	92.24

maintaining catalytic stability. XRD patterns further demonstrated that the crystalline structure of HZSM-5 was preserved after metal loading, ensuring the retention of shape-selective properties favorable for ethylene formation.

Nitrogen adsorption–desorption analysis showed a slight reduction in surface area and micropore volume after metal impregnation due to partial pore blocking; however, the presence of mesopores was maintained. This hierarchical structure facilitates improved mass transfer and reactant diffusion, particularly at lower reaction temperatures, thereby enhancing ethanol conversion. Most importantly, PZC analysis revealed a significant increase in surface acidity upon metal incorporation, especially for W-modified catalysts, as evidenced by the lower pH_{PZC} values. The stronger acidic character of W/HZSM-5 promotes efficient ethanol adsorption and dehydration to ethylene, explaining its superior conversion and selectivity.

At higher tungsten loading (2%W/HZSM-5), excessive acidity likely leads to partial pore blockage and over-acidification, resulting in a slight decrease in ethylene selectivity. Therefore, the optimal performance of 1%W/HZSM-5 arises from a synergistic combination of preserved zeolite structure, suitable pore architecture, and well-balanced surface acidity, as confirmed by the catalyst characterization results.

4. Conclusions

The modification of the HZSM-5 catalyst by using the impregnation metal (Ag, Co, W) significantly improved catalytic performance in the dehydration reaction of bioethanol to bioethylene. The highest ethylene conversion and selectivity (98.20 and 99.88%, respectively) at 300 ℃ were obtained for the 1%W/HZSM-5 catalyst. The increase of the tungsten loading from 0.5% to 1% notably enhanced both ethanol conversion and ethylene selectivity; further increment to 2% led to a slight decline in selectivity.

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Patent

Patent of HZSM-5 modification was registered (No. P00202411926 and P00202411927) under the Ministry of Law and Human Rights of Republic Indonesia.

CRedit Author Statement

Author Contributions: D. A. Risnawati: Investigation, Data Collection, Analysis, Draft Preparation, Visualization; N. Y. Pradana: Methodology, Investigation, Data Collection, Analysis, Draft Preparation, Visualization; Rochmadi: Methodology, Supervision, Review, Validation, Resource; I. Prasetyo: Methodology, Supervision, Review, Validation, Resource; D. D. Saputra: Review & Editing, Project Administration, Resource; H. Pranamuda: Supervision, Review, Project Administration, Resource; S. Tandio: Supervision, Review, Resource; T. Ariyanto: Methodology, Supervision, Review, Validation, Project Coordinator. All authors have read and agreed to the published version of the manuscript.

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