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RESEARCH PAPER

Selective Propylene Production from Methanol Using Monolithic Ge-Modified ZSM-5 Nanocatalysts

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ABSTRACT

In this study, we investigated the selective production of propylene from methanol using monolith-structured ZSM-5 and germanium-modified ZSM-5 nanocatalysts within a fixed-bed reactor system. Optimal reaction conditions were established as 500 °C, 1 bar pressure, and a weight hourly space velocity (WHSV) of 15 h^{-1}, with methanol as the feedstock. To assess the physical and chemical characteristics of the pelletized parent, Ge-modified, and monolith-structured HZSM-5 nanocatalysts, we utilized various analytical techniques, including X-ray diffraction (XRD), scanning electron microscopy (SEM), Brunauer-Emmett-Teller (BET) surface area analysis, and ammonia temperature-programmed desorption (NH3-TPD). NH3-TPD results indicated a reduction in acidity for the Ge-modified HZSM-5 nanocatalyst, attributed to the partial elimination of strong acid sites. XRD patterns confirmed the presence of the washcoat on the monolith-structured support. Additionally, SEM images of the Ge-modified and monolith-structured HZSM-5 nanocatalysts showed no change in the crystallinity of HZSM-5, while demonstrating a uniform nanocatalyst coating within the channels of the monolith-structured support. The most effective modified nanocatalyst was achieved by incorporating 0.1 wt% germanium into ZSM-5, which resulted in a substantial enhancement of propylene selectivity by 53% and yield by 22.1%. Among the monolith-structured nanocatalysts, variations with single-layer, double-layer, and triple-layer coatings of HZSM-5 were prepared. The single-layer HZSM-5 monolith-coated nanocatalyst exhibited the most significant improvements, with propylene selectivity increasing by 55% and yield by 28.4%. These improvements were attributed to enhanced internal diffusion and reduced mass transfer resistances within the monolith channels, leading to shorter residence times and reduced aromatic formation

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INTRODUCTION

Ethylene and propylene, as light olefins, are critical feedstocks in the polymer and fiber industries. Ethylene is a major chemical consumed in large quantities, while propylene is essential for producing polypropylene, propylene oxide, acrylonitrile, phenol, and various other chemicals. Its extensive applications span multiple industries, including automotive, construction, packaging, medical, and electronics. However, the rising demand for propylene has driven up its price. Traditionally, olefins are produced via the thermal

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cracking of naphtha or other light petroleum fractions using steam cracking technology. In contrast, zeolite-based technologies, particularly the methanol-to-olefins (MTO) process, offer an alternative route for olefin production from renewable resources [1–4].

The product ratio of ethylene and propylene in the MTO process is influenced by reactor operating conditions, primarily temperature and pressure. To enhance propylene selectivity, selective catalysts such as ZSM-5 and SAPO-34 are employed, with ZSM-5 exhibiting superior performance due to its structural characteristics. Modifying ZSM-5 catalysts with metals and semi-metals is anticipated to further improve propylene selectivity, water tolerance under high temperatures and pressures, reduce deactivation rates, and increase mechanical strength [5–8].

Zeolite catalysts possess a crystalline aluminosilicate structure with three-dimensional nanometer-sized channels and cages, resulting in high porosity and a large surface area. With typical channel dimensions, intersections, and cages below 2 nm, zeolites are categorized as microporous materials, providing unique catalytic properties [8].

Catalyst modification with promoters is an effective strategy to enhance zeolite catalyst performance. In the methanol-to-propylene (MTP) reaction, the presence of weak acid sites is critical as they act as active sites for olefin production [9]. These weak acid sites are essential for minimizing the formation of alkanes and aromatics, thereby improving stability and anti-coking properties compared to strong acid sites. Side reactions on active sites contribute to coke formation, which ultimately leads to catalyst deactivation over prolonged reaction times [10].

The presence of weak acid sites in ZSM-5 catalysts extends their lifespan by mitigating coke formation, unlike strong acid sites. Since acidity significantly impacts the MTP reaction, controlling the balance between weak and strong acid sites is crucial for optimal performance. Promoters are instrumental in achieving this balance by introducing additional acid sites on the catalyst surface and enhancing its performance. The incorporation of appropriate promoters [11,12] and the renovation of mesopores [13,14] in ZSM-5 catalysts enhance propylene selectivity and overall performance due to modifications in acidity and porosity. Notably, promoters not only reduce strong acid sites but also diminish aromatics formation.

This study focuses on the modification of zeolite catalysts using a germanium (Ge) promoter for the catalytic conversion of methanol into light olefins, particularly propylene. Additionally, we investigated the selective production of propylene from methanol using monolith-structured HZSM-5 catalysts within a fixed-bed reactor system.

The novelty of this research lies in the development of a Ge-modified ZSM-5 nanocatalyst, which significantly enhances propylene selectivity and yield by optimizing acidity and reaction pathways. Additionally, the introduction of monolith-structured HZSM-5 nanocatalysts with different coating layers improves internal diffusion and reduces mass transfer resistance, leading to a more efficient methanol-to-propylene conversion. These advancements provide new insights into catalyst design for selective light olefin production.

MATERIALS AND METHODS

The catalyst preparation involved the use of chemicals sourced from Sigma-Aldrich. The chemicals employed in the process were as follows: TEOS (tetraethyl orthosilicate, >99.0%), TPAOH (tetra propyl ammonium hydroxide, 1.0 M in water), NaOH (sodium hydroxide, 5.0 M in water), H_2SO_4 (sulphuric acid, 1% in water), $Ge(NO_3)_2$ (germanium nitrate, >99.0%), colloidal silica (Ludox AS-40) (40 wt. % in H_2O), and sodium aluminate ($NaAlO_2$).

Synthesis of HZSM-5 zeolite

ZSM-5 synthesis involves the use of feedstock and seeding gels to produce 5 µm crystals with a silicon-to-aluminum ratio of 16. For the seeding gel, colloidal silica (Ludox AS-40) (40 wt. % in H_2O), sodium hydroxide, tetrapropylammonium hydroxide (TPAOH), and deionized water were utilized. The seeding gel was aged at 100°C overnight to allow for proper development.

In the feedstock preparation, sodium aluminate ($NaAlO_2$), sodium hydroxide (NaOH), colloidal silica, and deionized water were combined. The seeding solution was then mixed with the feedstock gel, and the resulting mixture was placed in an autoclave and maintained at a temperature of 160°C for 24 hours. Subsequently, the product was washed, filtered, and dried, after which the template was removed. This involved a gradual solid heating process, increasing at a rate of 5°C per minute, until reaching 550°C in a furnace.

Finally, the calcination of the ammonium form of ZSM-5 was carried out at a temperature of 550°C for 8 hours to obtain H-ZSM-5.

Germanium - HZSM-5 NanoCatalysts Preparation

The modification of catalysts was carried out using the incipient impregnation technique. The pore filling method was employed, which is a straightforward approach where the metal precursor was poured onto the catalyst sample. To ensure the impregnation process was successful, all catalysts were first calcined at 550°C for 3 hours and then placed into a desiccator to prevent moisture absorption.

The incipient pore volume required for impregnation was determined based on 1 gm of the catalyst by carefully adding deionized water drop by drop. This volume of water was used to create the solutions containing metals and semi-metal promoters. Specifically, a $Ge(NO_3)_2$ solution with the necessary loading amount was prepared and added to the powdered catalyst. Subsequently, all impregnated samples were dried at 100°C and calcined at 400°C for 12 hours.

To prepare the catalysts for testing in the fixed-bed reactor system, all samples were pelletized, crushed, and sieved to achieve a size range of 0.5-1 mm.

Monolith Nano Catalysts Preparation

The application of zeolite coating on a structured support can be achieved through various methods, including wash coating, hydrothermal coating, or a combination of both [15,16] . For this study, a structured nanocatalyst was prepared using the dip coating method, falling under the wash coating technique, on a honeycomb cordierite monolith support with 400 CPSI (cells per square inch).

The dip coating process involved three steps. In the first step, the cordierite monolith support was washed in a 5 wt% HNO_3 DI water solution for 20 minutes, dried at 110°C for 6 hours, and then calcined at 550°C for 6 hours. Next, a slurry was prepared in the second step, comprising 20 wt% ZSM-5 zeolite and 1 wt% colloidal silica (Ludox AS-40) in 20 grams of DI water. This slurry was stirred for 6 hours on a magnetic stirrer at 600 rpm at ambient temperature and further treated in an ultrasonic bath for 15 minutes.

For the final step, the monolith was dipped in the prepared slurry for 3 minutes and then removed, with excess slurry eliminated by passing dry air through the monolith channels. The zeolite-coated monolith was subsequently dried at 110°C with a ramp rate of 2°C/min in a rotating oven for 12 hours, followed by calcination at 500°C with a ramp rate of 3°C/min for 4 hours. Ultrasonic treatment for 1 minute was applied to the prepared structured nanocatalyst to enhance adhesion strength [94,95], resulting in weight loss.

To increase the zeolite coating thickness, the monolith was dipped two to three times in the leftover nanocatalyst slurry. The adhesion of the nanocatalyst coating was assessed based on monolith-coated zeolite samples. The performance of the prepared monolith-structured nanocatalyst was then evaluated in a fixed-bed reactor system.

Experimental System

Fig. 1 illustrates the process diagram of the fixed-bed reactor setup, which consists of four sections: (i) feed section, (ii) preheater, (iii) reactor section, and (iv) product collection and separation section.

The feed section is designed to supply the feed during the reaction under controlled pressure and flow rate. It comprises a methanol storage tank, a methanol feed pump, and an inert (nitrogen) cylinder. The feed tank is filled with approximately one-third of feed methanol and connected to an HPLC series 1 pump, operating between flow rates of 0.10 to 0.64 ml/min. Nitrogen flow is supplied during the reaction with a pressure set point of 5 bar, initiated when the reactor temperature reaches 300°C. This pretreatment helps remove any impurities trapped inside the pores of the nanocatalyst.

Methanol fed by the HPLC pump is preheated to 100°C in the preheater, with heat insulation provided from the preheater to the furnace. Methanol and nitrogen are mixed in the heated inlet line before entering the reactor, ensuring a homogenous feed mixture. Insulation is applied to maintain a stable temperature during operation.

The reactor, made of stainless steel with an internal diameter of 21 mm and an overall length of 300 mm, contains the nanocatalyst sample placed in the mid-section. Two thermocouples are attached to the reactor, one indicating the wall temperature and the other placed in the center of the nanocatalyst bed. Nanocatalyst bed formation inside the reactor involves strategically loading SiC particles of different sizes, ensuring uniform feed distribution.

The product separation section is designed to separate the product stream into liquid and gas. It includes a condenser and a gas-liquid separator column, both connected to a water circulating tank with a temperature set at 5°C. The cooled water flows through the condenser and then to the GLS column. The condensed liquid is collected for further analysis, while the gas stream is separated in the GLS and directed through the heated outlet line connected to the GC.

Gas chromatography

In this study, gas and liquid analysis were performed using the Agilent 7890B GC. The GC was connected online for the examination of gas samples. It is equipped with a TCD (thermal conductivity detector) featuring a GASPRO column (60m X 320µm) and an FID (flame ionization detector) with an INNOWAX column (30m X 320µm X 0.5µm) for gas and liquid samples, respectively.

The GC was connected to three cylinders containing H2, He, and Air gases. Helium served as the carrier gas in our GC system. To initiate the GC, all cylinders were opened, and the oven temperature was set at 250°C. Prior to sample analysis, a blank run was conducted to eliminate any extraneous peaks in the samples.

To facilitate data analysis, we developed two methods: the first method was the online gas method for gas sample analysis, and the second method was the online liquid method for liquid sample analysis. Before starting each run for analysis, the appropriate sample information was provided to ensure accurate results.

Nanocatalyst Characterization Methods

The successful production of propylene from the methanol process relies on the physical, chemical, thermal, and structural properties of the zeolite nanocatalyst. To analyze the obtained results effectively, a comprehensive understanding of the nanocatalyst properties is essential, and this can be achieved through various characterization

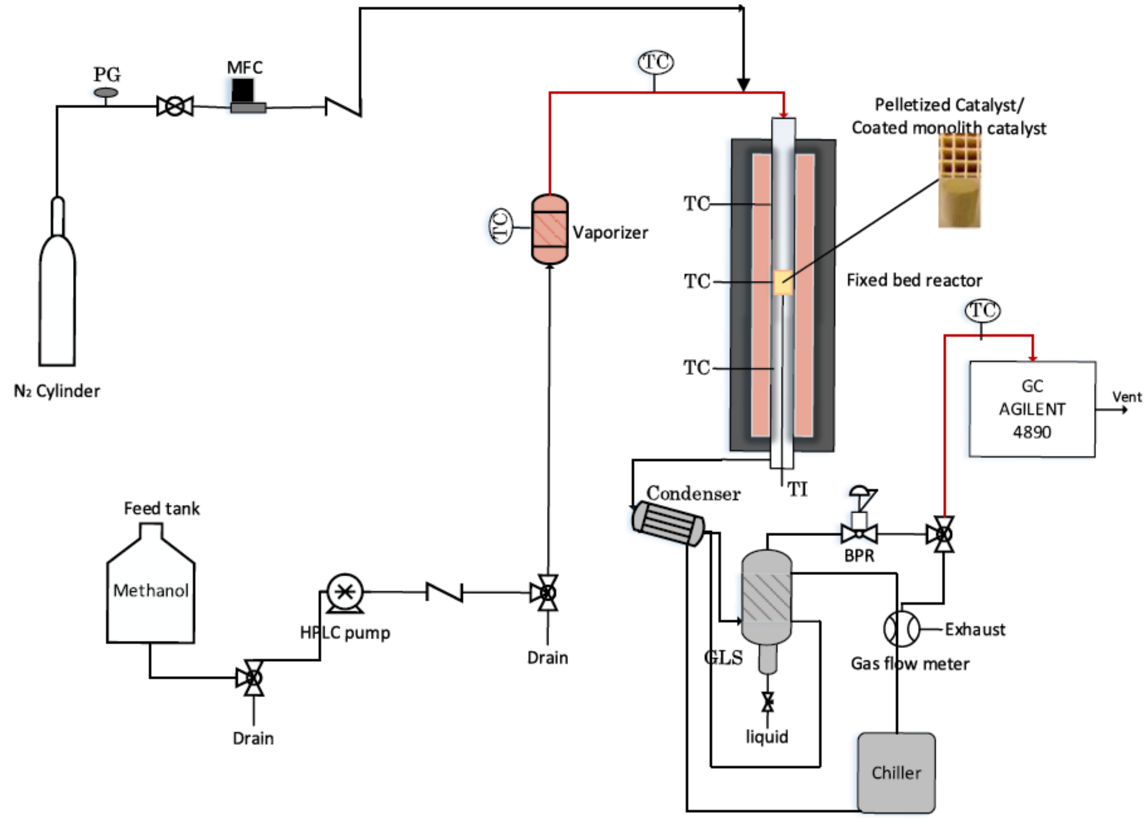

Fig. 1. Fixed bed reactor system.

methods. Hence, all zeolite, modified zeolite, and monolith-coated zeolite ZSM-5 nanocatalysts were subjected to characterization for their physical and chemical properties, including surface area, pore volume, pore size distribution, crystallinity, acidity, and surface morphology.

X-ray Diffraction (XRD)

The measurement of the degree of crystallinity in zeolite samples is a critical aspect assessed through X-ray diffraction (XRD), which is an important technique. The crystallinity is a fundamental property for zeolite nanocatalysts, and to be considered a genuine zeolite, the sample must exhibit a well-defined MFI structure, characteristic of standard zeolite ZSM-5 nanocatalysts.

For XRD analysis, a Rigaku Miniflex diffractometer was utilized. Each zeolite sample was placed on a small glass slab using a gel, and then positioned inside the diffractometer. The analysis involved employing monochromatic Cu Kα radiation with a wavelength (λ) of 1.5406 * 10^-1 nm, operating at room temperature, 50 mA current, 2θ in the range of 5° to 50°, with a step size of 0.02°, a scan rate of 3° per minute, and an electrical voltage of 10 kV.

Temperature Programmed Desorption (NH_3-TPD)

To measure the acidity, Ammonia Temperature Programmed Desorption (NH_3-TPD) analysis was performed, which plays a crucial role in determining the product distribution in the MTP process for a zeolite nanocatalyst. The USA-made equipment AutoChem II 2029 analyzer, equipped with an online TCD, was utilized for conducting the TPD analysis on all samples.

Before the TPD analysis, all samples were subjected to calcination at 500°C for 6 hours in a furnace to eliminate any impurities. For the analysis, 0.05-0.1 gm of nanocatalyst samples were loaded inside a U-shape quartz tube and then degassed at 500°C for 3 hours by flowing Argon at 30 ml/min. Subsequently, the sample inside the tube was cooled to 120°C using a 5% NH_3/He gas mixture with a flow rate of 50 ml/min. The system was purged using He at 100°C with a flow rate of 50 cm3/min to ensure the removal of any traces of NH_3 gas phase and adsorbed ammonia in the nanocatalyst sample.

The nanocatalyst bed temperature was gradually increased to 750°C for the desorption analysis, with a ramp rate of 10°C per minute. As the temperature elevated to 750°C, the ammonia was desorbed, and its concentration in the effluent was monitored using the Thermal Conductivity Detector (TCD).

BET Surface area

The surface area of a zeolite nanocatalyst is a critical property that significantly influences gas adsorption and catalytic activity. It provides valuable insight into the available surface for catalytic reactions. The Brunauer-Emmett-Teller (BET) method is commonly employed for surface area analysis, wherein the nanocatalyst pores are envisioned as cylindrical capillaries with varying shapes, sizes, and lengths.

Understanding the pores of the zeolite nanocatalyst is essential for comprehending shape selectivity. The BET surface area and pore volume of different samples were assessed using the Micromeritics ASAP 210 analyzer through N2 adsorption at 77 K. Prior to analysis, all samples were calcined at 500°C for 6 hours to eliminate any impurities. Subsequently, 0.2 grams of the sample was degassed using N2 flow at 300°C for 3 hours to remove any adsorbed moisture on the pores and surface.

The BET method was employed to calculate the total specific surface area within the relative pressure (p/po) range of 0.0 to 0.25. Furthermore, the total pore volume and pore size distribution were estimated using the Barrett-Joyner-Halenda (BJH) method, based on adsorbed nitrogen at N2 relative pressure (p/po) 0.99. These analyses provide valuable information about the surface area and porosity, which are crucial factors in determining the catalytic performance of the zeolite nanocatalyst.

Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (SEM) is a powerful technique employed to examine the surface morphology of the nanocatalyst. It provides clear and detailed images of specimens, ranging from visible objects to nanometer-scale structures.

For SEM-EDX analysis, the nanocatalyst sample was spread on a pin stub using copper tape. To prevent any charge build-up during the analysis and enhance the secondary electron signal, a gold coating was applied to the samples using the Cressington sputter coater for 1.5 minutes. This process enables better contrast and allows for high magnification, up to 100,000 times, ensuring detailed visualization of the sample's surface.

Nanocatalyst Evaluation system and method

The catalytic activity of each sample for methanol conversion and propylene selectivity was assessed using a fixed-bed reactor system made of stainless steel. The reactor had an internal diameter of 21 mm and an overall length of 300 mm, with a heating length of 200 mm.

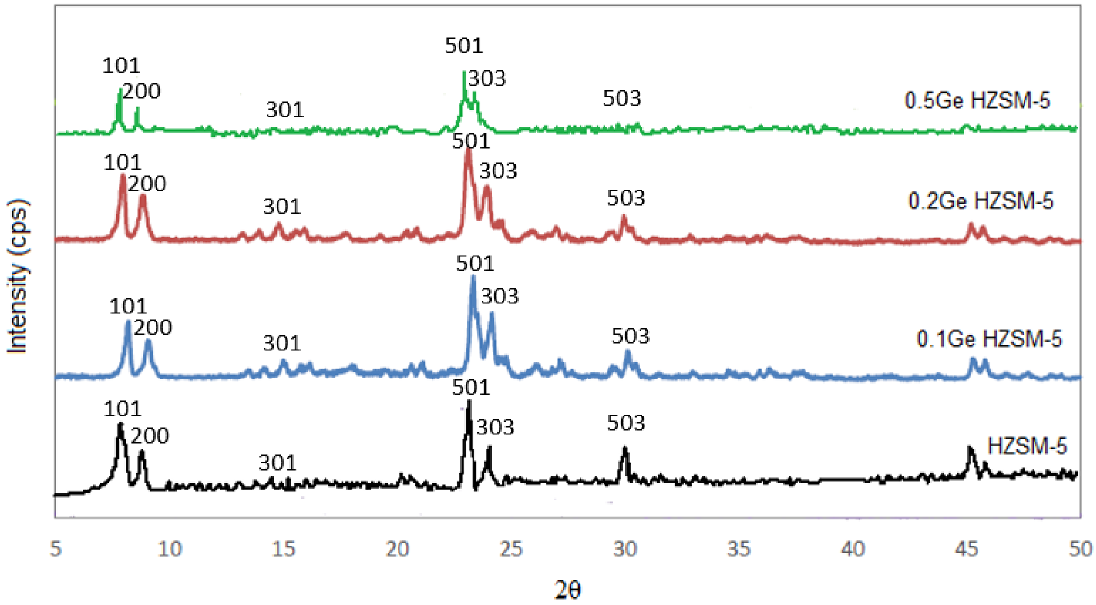

Fig. 2. XRD patterns of HZMS-5, 0.1Ge HZSM-5, 0.2Ge HZSM-5 and 0.5 Ge HZSM-5 samples.

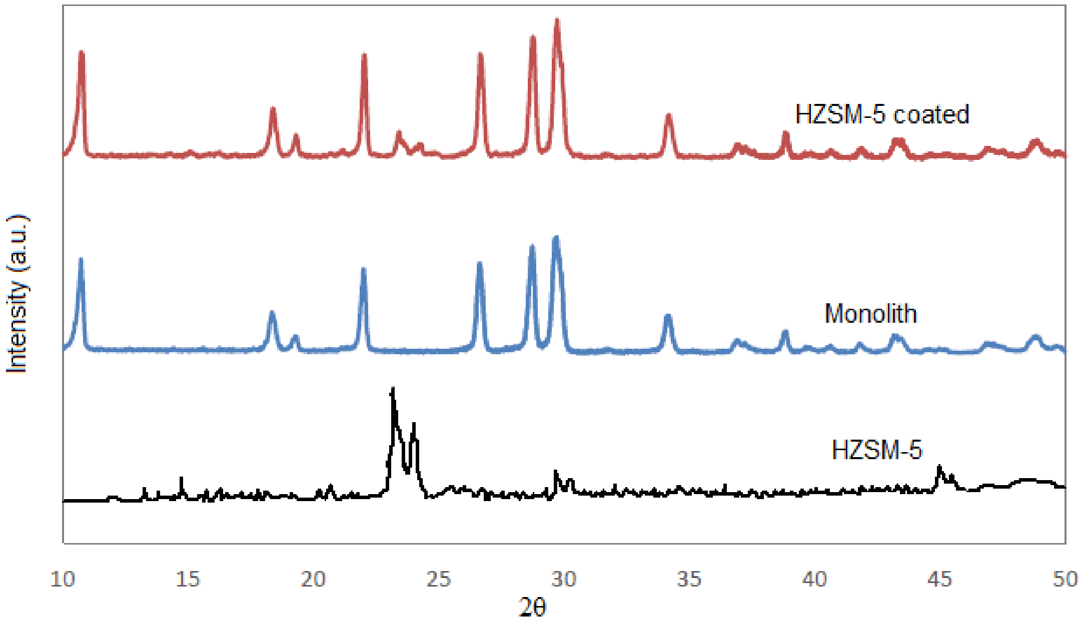

Fig. 3. Comparison between XRD patterns of HZMS-5, Monolith and HZMS-5 coated monolith.

Its maximum operating temperature was set at 600°C, and the pressure was maintained at 20 bar. During the nanocatalyst evaluation, the parent and modified powder zeolite nanocatalysts were filled into a die and pelletized under high pressure. The resulting pellets were subsequently crushed and sieved to obtain mesh particles ranging from 0.5 to 1 mm.

For the tests, 1 g of the mesh nanocatalyst was loaded into the middle of the isothermal zone of the reactor. An hydrothermally and mechanically stable zeolite-coated cordierite honeycomb monolith with 400 CPSI was evaluated in the reactor system under conditions of 500°C, 1 bar pressure, and 15 h-1 WHSV (weight hourly space velocity).

The reactions were conducted for 2.5 hours, and samples were analyzed three times at 30, 90, and 150 minutes using an online GC-7890B equipped with both a TCD (thermal conductivity detector) with a GASPRO column (60m X 320µm) and an FID (flame ionization detector) with an INNOWAX column (30m X 320µm X 0.5µm).

To determine the performance metrics, methanol conversion, propylene selectivity, and yield were calculated as follows: Conversion (%) = (Mass of methanol in – Mass of methanol out) / Mass of methanol in * 100 Gas Selectivity (%) = Mass of product (gas) / Mass of gaseous hydrocarbons Yield (%) = Mass of product / Mass of methanol feed.

RESULTS AND DISCUSSION

XRD results

The identification of the crystalline phase was performed through XRD analysis. Fig. 2 displays the XRD patterns of HZSM-5, 0.1Ge HZSM-5, 0.2Ge HZSM-5, and 0.5 Ge HZSM-5. The pattern for HZSM-5 clearly exhibits the typical MFI structure of standard zeolite ZSM-5 nanocatalyst, with main peaks observed at 2θ values of 7.9, 8.2, 23.1, 23.3, 23.9, and 29.9 degrees. Notably, no amorphous impurity is detected in the samples, as confirmed by the XRD pattern.

The intensity of diffraction peaks for 0.1Ge HZSM-5 and 0.2Ge HZSM-5 nanocatalysts is nearly identical, indicating no significant change in crystallinity after Ge modification on the parent HZSM-5 nanocatalyst. However, a slight reduction in crystallinity is observed in the 0.5 Ge HZSM-5 sample, as evidenced by a drop in intensity. This drop suggests a minor effect on crystallinity after loading 0.5 wt% Ge on the HZSM nanocatalyst.

Fig. 3 illustrates XRD patterns for zeolite HZSM-5, honeycomb cordierite monolith support, and HZSM-coated monolith structured nanocatalysts. The XRD pattern obtained for the zeolite-coated monolith exhibits additional peaks highlighted on

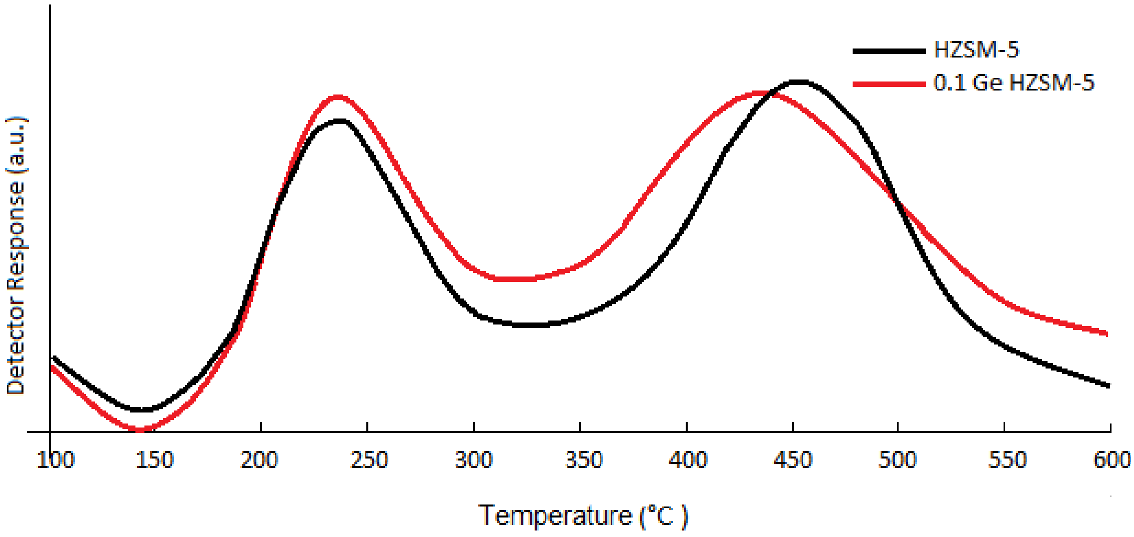

Fig. 4. NH3-TPD profile of HZSM-5 and 0.1Ge HZSM-5.

the pattern, confirming the presence of the zeolite HZSM nanocatalyst on the monolith support.

NH_3-TPD Measurements

Fig. 4 presents a comparison of NH_3-TPD profiles between the parent HZSM-5 nanocatalyst and the 0.1Ge modified HZSM-5 nanocatalyst. The Ge-modified nanocatalyst exhibits a TPD profile similar to that of the parent nanocatalyst, but there is a noticeable shift of the strong acid site peak from

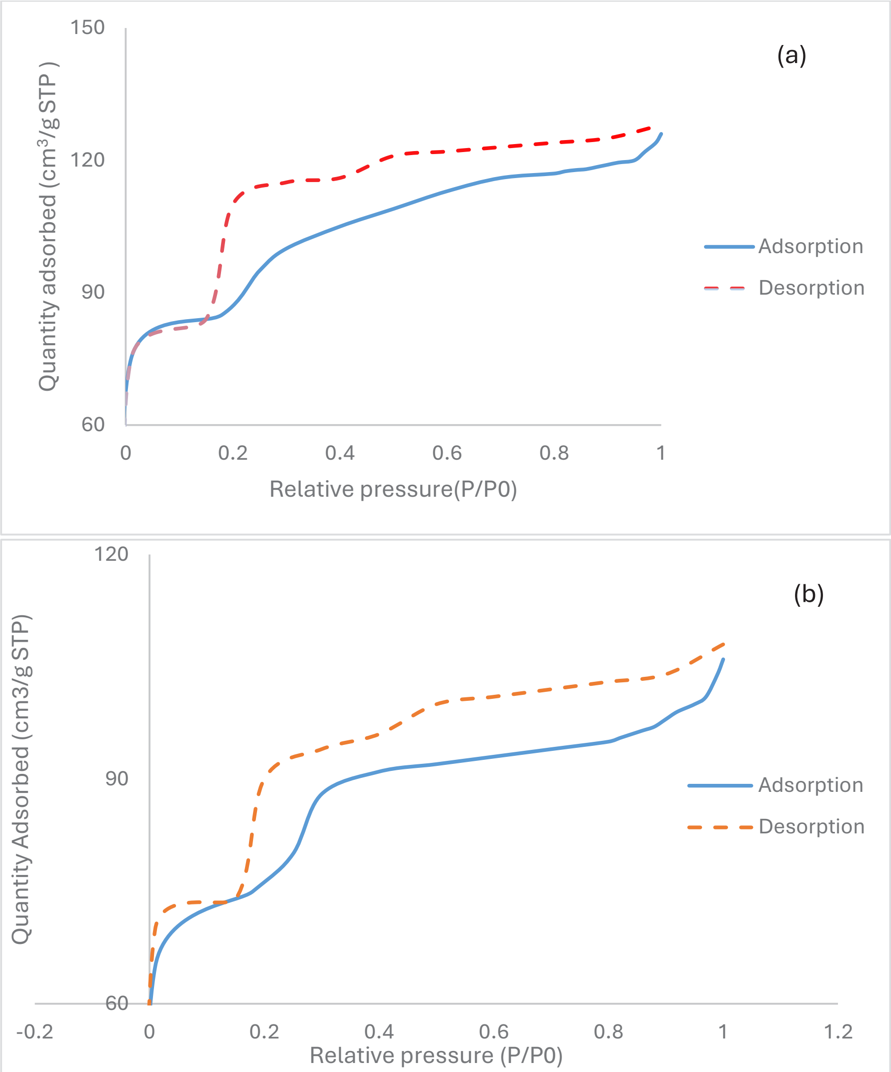

Fig. 5. N2 adsorption desorption plot for a) HZSM-5, b)0.1Ge HZSM-5.

Table 1. Textural properties resulted by BET analysis.

Sample	A_{BET} (m^2/g)	A_M (m^2/g)	V_{micro} (cm^3/g)	V_{meso} (cm^3/g)	V_{total} (cm^3/g)	D_{AA} (nm)
HZSM-5	363.6	321	0.145	0.051	0.212	2.6
0.1Ge HZSM-5	352.7	312.8	0.123	0.065	0.215	2.3

453 to 442 °C. The acidity obtained for HZSM-5 is 0.064 mmol/g of nanocatalyst, while for 0.1Ge HZSM-5, it is 0.041 mmol/g of nanocatalyst. These results indicate that there is a partial elimination of strong acid sites after the Ge modification of the zeolite HZSM-5 nanocatalyst.

BET Surface Area, Pore volume and Pore size Distribution. Table 1 presents the BET surface area results. Fig. 5 displays the N2 adsorption-desorption isotherm plots and pore size distribution for HZSM-5 and 0.1Ge HZSM-5. The comparison between the parent and 0.1Ge modified zeolite HZSM-5 reveals only a slight change in the total surface area, micro-pore surface area, and pore volume

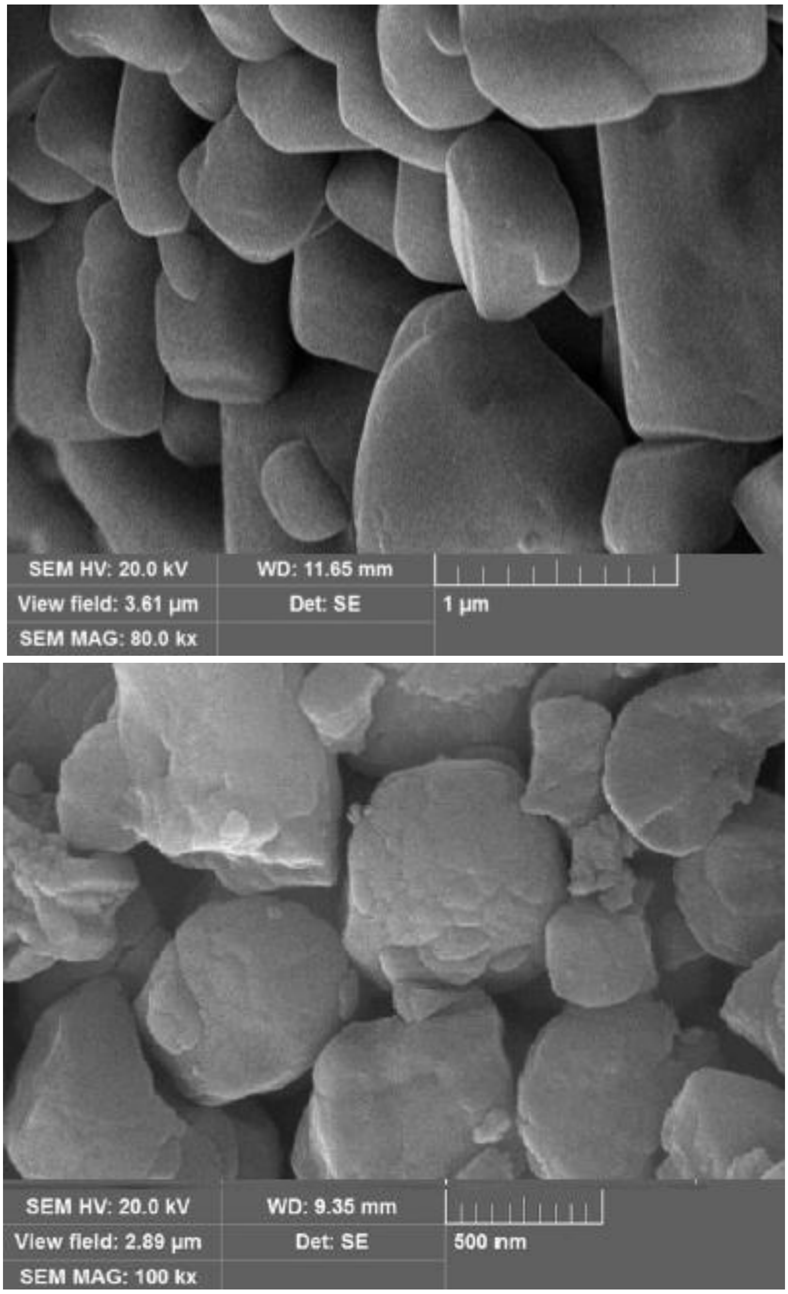

Fig. 6. SEM images of a) HZSM-5 and b) 0.1Ge HZSM-5.

of the Ge-modified HZSM-5 in comparison to the parent nanocatalyst. This indicates that there is no significant alteration in the MFI structure of the zeolite nanocatalyst due to Ge modification.

However, there is an increase in the mesoporosity and a decrease in the average pore diameter of the Ge-modified HZSM-5, which leads to a reduction in aromatics formation. It is believed that the aromatics formed during the reaction diffuse back and are likely to dissociate into olefins, thus enhancing the olefins selectivity after the Ge modification of the HZSM-5 nanocatalyst.

SEM Analysis

Fig. 6 displays the SEM images of the parent and 0.1Ge modified HZSM-5 nanocatalysts. These images emphasize the high crystallinity of both zeolite samples, with cubical or elliptical-shaped crystals and a uniform size distribution.

Fig. 7 presents the surface morphology of the honeycomb monolith support. The images clearly demonstrate the macroporous nature of the monolith support, providing ample space for zeolite diffusion and adhesion without any abrasion.

In Fig. 8, the SEM images depict the single-layer monolith coated zeolite HZSM nanocatalyst. It is evident that the surface morphology of the zeolite remains unchanged after coating with 1% binder (Ludox AS-40). The zeolite is uniformly dispersed on the monolith's surface, leaving no significant areas uncoated.

Fig. 9 showcases the SEM images of the double-layer and triple-layer monolith coated HZSM nanocatalysts. It can be observed that the coating thickness increases from single to double layer and then to triple layer. The zeolite coating thickness for single-layer, double-layer, and triple-layer monolith-coated HZSM-5 nanocatalysts is measured to be 4.2 µm, 6.3 µm, and 11.9 µm,

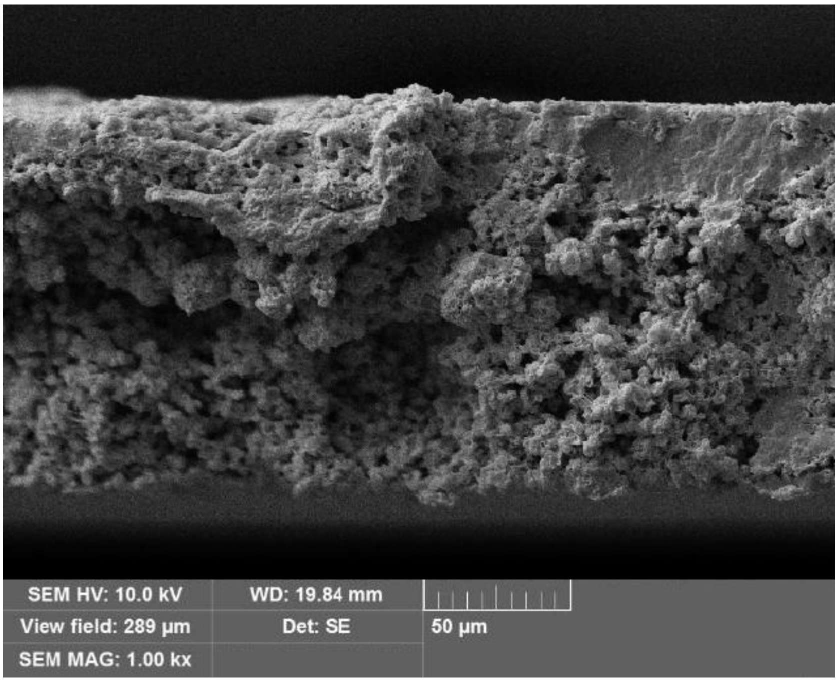

Fig. 7. surface morphology of the honeycomb monolith support.

respectively.

TEM Analysis

TEM images of the H-ZSM-125 are shown in Fig. 10.

The morphology of the synthesized ZSM-5 zeolite powders was analyzed using Transmission Electron Microscopy (TEM). Fig. 10 illustrates the characteristic shape of the synthesized H-ZSM-5 zeolite nanocrystals. As shown in Fig. 10, the ZSM-5 zeolite exhibited a nanosized spherical and benzene-like crystal structure, which is attributed to the fact that smaller particles have a higher surface area. The spherical shape helps minimize the particle's surface energy, reaching its lowest possible value. The zeolite crystal particles showed a uniform size distribution, with an average size of approximately 30nm.

Nanocatalyst Evaluation

This section presents the catalytic activity of zeolite, modified zeolite, monolith-coated zeolite, and modified monolith-coated zeolite nanocatalysts. The performance of each nanocatalyst type is thoroughly examined. Additionally, a comparison is drawn among

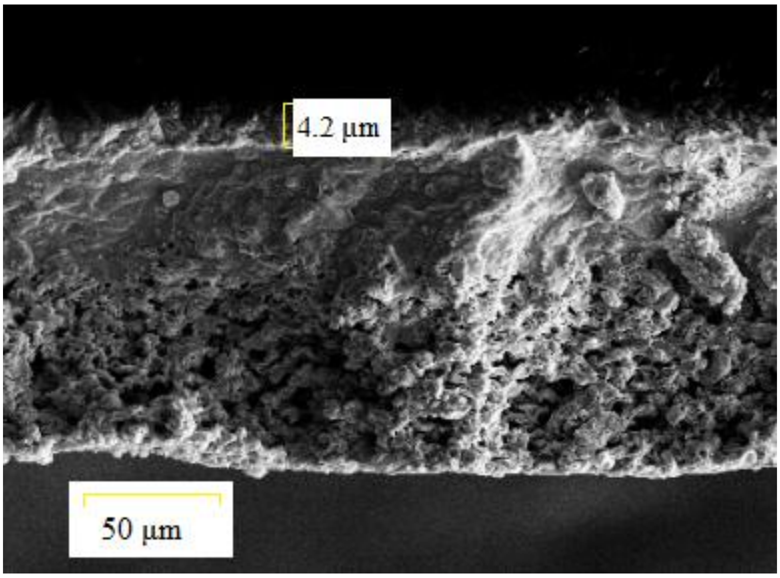

Fig. 8. SEM image of the single layer monolith coated zeolite HZSM nanocatalyst.

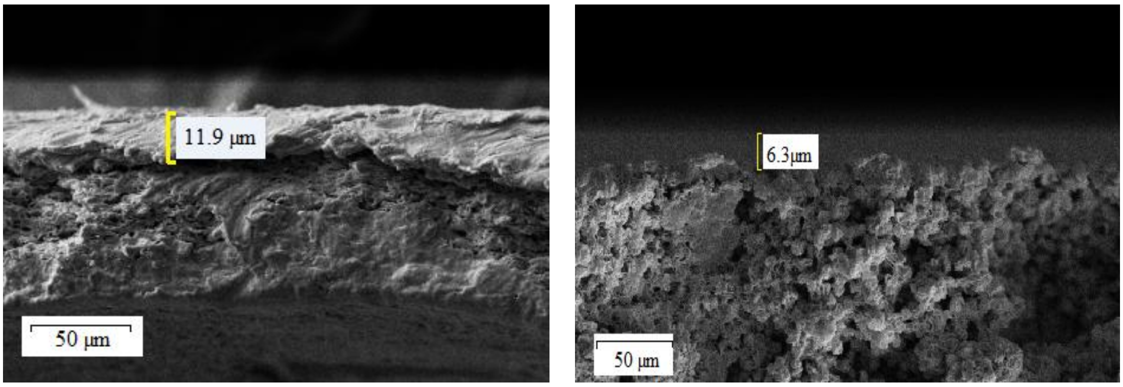

Fig. 9. SEM images of (a) double layer, (b) triple layer HZSM-5 coated monolith nanocatalyst.

the parent, Ge-modified, and monolith-coated nanocatalysts based on a 40-hour reaction duration. All experiments were conducted in a fixed-bed reactor system, and the typical process variables, such as temperature, pressure, and space velocity, were carefully controlled throughout the reactions.

Effect of Temperature and Pressure

The catalytic activity of a zeolite nanocatalyst is significantly influenced by temperature and pressure. In a packed bed pelletized nanocatalyst, a pressure drop occurs, leading to side reactions, particularly olefin oligomerization, which results in increased aromatics generation and reduced propylene selectivity. Temperature plays a crucial role in product distribution during the conversion of methanol to hydrocarbons. Higher temperatures favor selectivity due to increased cracking reactions [17,18]. However, elevated temperatures can also cause methanol decomposition to methane.

To understand the effect of temperature and pressure on zeolite HZSM-5, experiments were conducted at different temperatures (400, 450, and 500 °C) and pressures (1, 2, and 3 bars) while maintaining a constant WHSV of 15 h-1. Fig. 10 illustrates the impact of temperature and pressure on methanol conversion and propylene selectivity. The results reveal that pressure has a prominent effect on both methanol conversion and propylene selectivity. Based on these findings, the reaction was carried out at 1 bar pressure.

For further investigation, the temperature range of 450 to 500 °C was considered, and ultimately, a temperature of 500 °C and a pressure of 1 bar were chosen for subsequent studies.

Effect of Weight Hourly Space Velocity

Space velocity is a critical parameter in the conversion of methanol to propylene. To understand its impact on zeolite nanocatalyst performance, experiments were conducted at optimum operating conditions, varying the space velocity. It is well-established that space velocity significantly influences the product distribution of hydrocarbons [19,20]. Lower residence time, achieved through low space velocities, generally enhances the selectivity of olefins. This is technically correct because high space velocities reduce the contact time of reactant molecules with the nanocatalyst's active sites, leading to decreased methanol conversion.

From the experimental results obtained, it can be concluded that the highest propylene yield was achieved at a WHSV of 15 h-1 (Fig. 12). At a space velocity of 11, propylene yield was lower compared to a space velocity of 15, while at a space velocity of 19, there was a significant drop in methanol conversion, resulting in decreased propylene yield. Based on these findings, a space

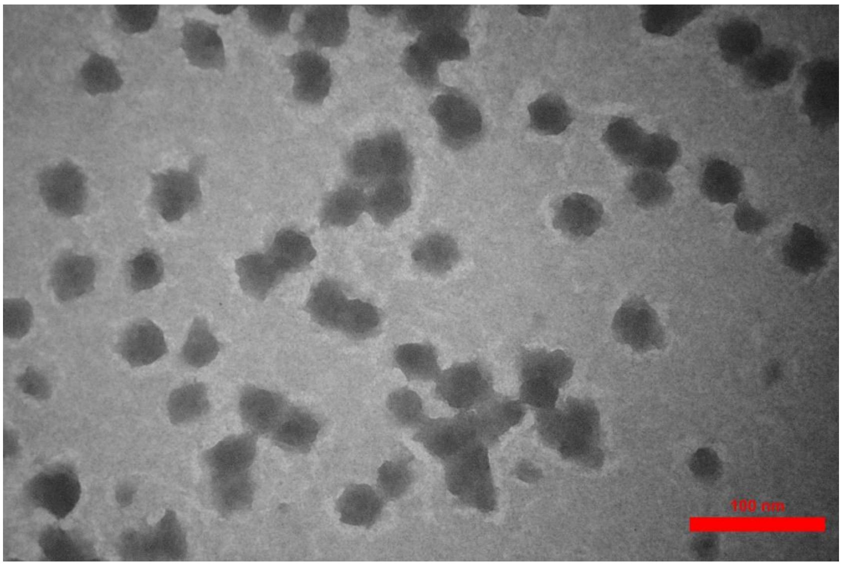

Fig. 10. TEM of nanosized ZSM-5 zeolite.

velocity of 15 h-1 was identified as the optimum condition for maximizing propylene yield.

Effect of HZSM-5 Modification

The HZSM-5 nanocatalyst was modified with Germanium using the incipient impregnation method. Nanocatalyst activity tests were conducted at a temperature of 500 °C, pressure of 1 bar, and WHSV of 15 h-1. It is widely known that the loading of promoters on zeolites can have both positive and negative effects on the results. As acidity plays a crucial role in the formation of various hydrocarbons in the MTP reaction, adjusting the ratio of weak to strong acid sites becomes essential to obtain the desired products. This can be achieved by using an appropriate promoter [21].

Table 2 illustrates the effect of Germanium on the HZSM-5 nanocatalyst with optimized loading and under optimum reaction conditions. Germanium loading was carried out at three levels: 0.1 wt%, 0.2 wt%, and 0.5 wt%. Fig. 13 shows that with an

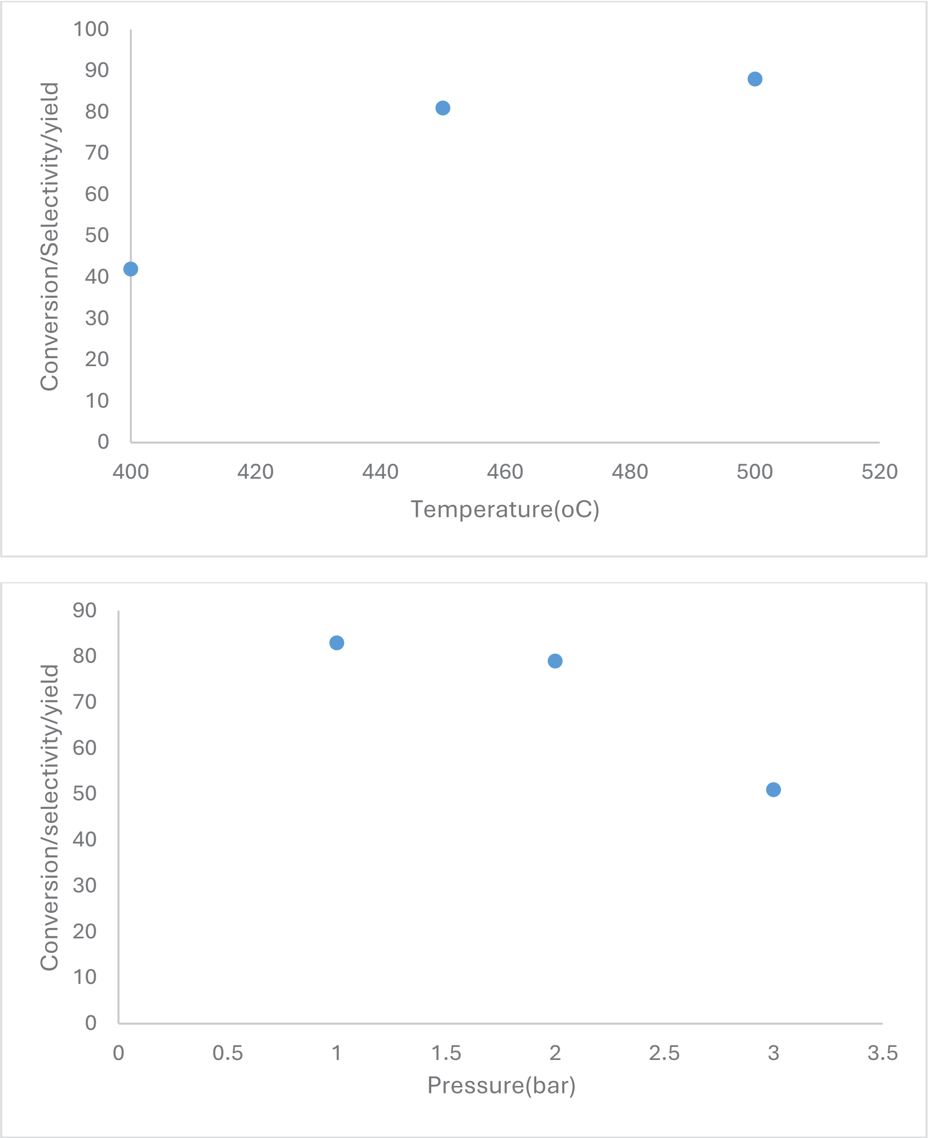

Fig. 11. Effect of temperature and pressure on methanol conversion, propylene selectivity and yield for HZSM at WHSV 15h-1.

increase in loading, there is a drop in methanol conversion, propylene selectivity, and yield. This decrease is attributed to a significant reduction in the acidity of the nanocatalyst. Hence, an optimized loading amount of 0.1 wt% Germanium was selected, as higher loading negatively affects the results by decreasing the number of acid sites present in the HZSM-5 nanocatalyst, leading to reduced methanol conversion.

The modified nanocatalyst with 0.1 wt% Germanium exhibits increased selectivity for olefins compared to the parent HZSM-5 nanocatalyst

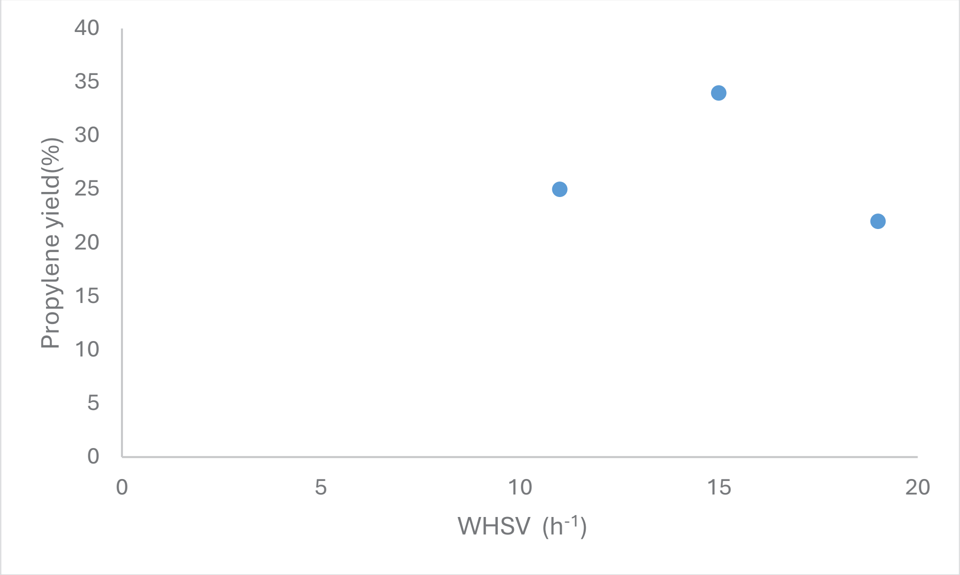

Fig. 12. The effect of space velocities on propylene yield.

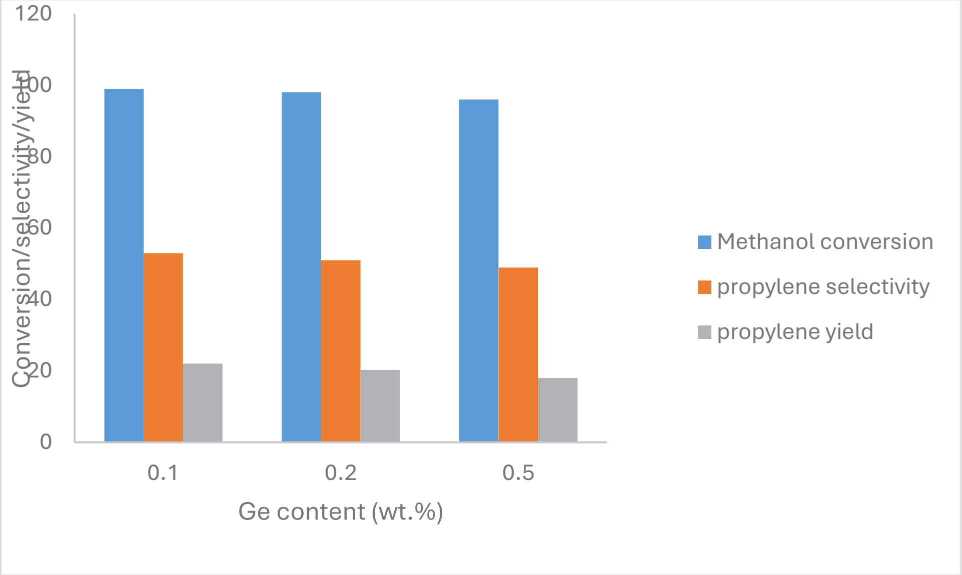

Fig. 13. Methanol conversion, propylene selectivity and yield comparison for Ge modified HZSM-5 nanocatalyst.

(Fig. 13). Particularly, there is an increase in the selectivity of ethylene with Germanium, indicating that hydrocarbon formation follows the alkene pool cycle [23,24]. The results suggest that the hydrocarbon formation follows the methylbenzene pool cycle, resulting in a significant decrease in aromatics due to the dissociation of polymethyl benzenes. This decrease in aromatics leads to slower nanocatalyst deactivation.

Overall, the addition of Germanium as a promoter to the HZSM-5 nanocatalyst has shown promising results, with an optimized loading of 0.1

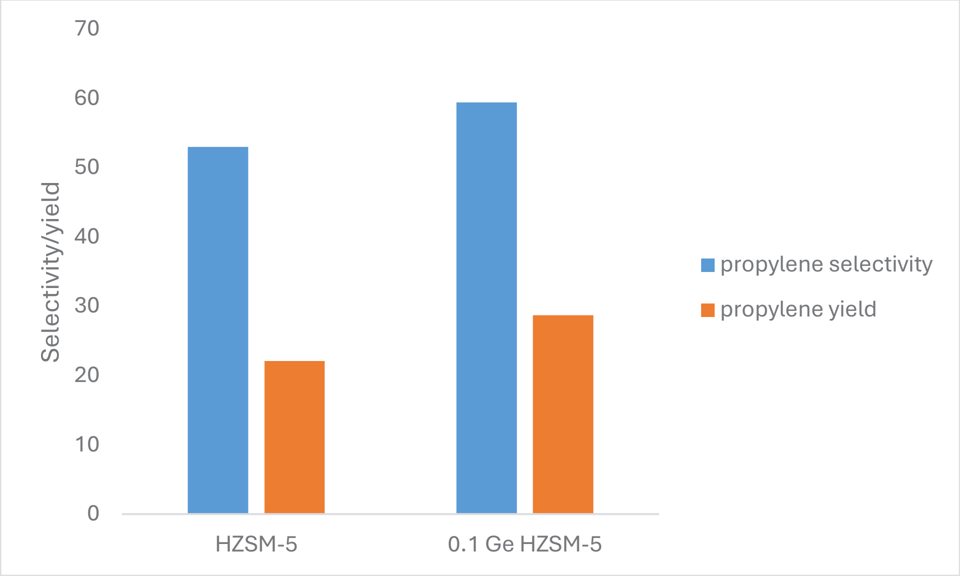

Fig. 14. Propylene selectivity and yield comparison for parent and modified HZSM-5 nanocatalysts.

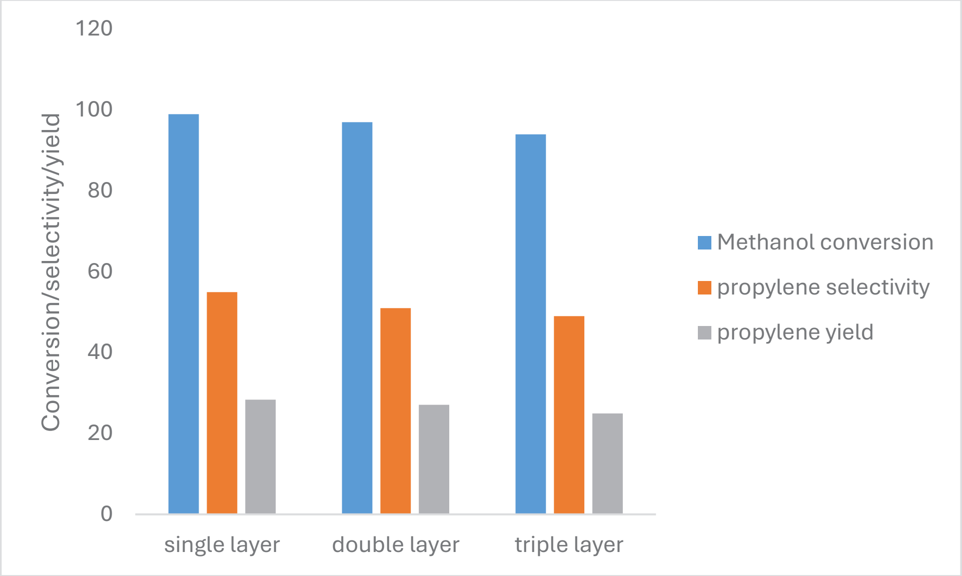

Fig. 15. Propylene selectivity and yield comparison for HZSM-5 coated on the monolith.

Table 2. effect of HZSM-5 and 0.1 Ge HZSM-5 coating on monolith.

	Single layer	Double layer	Triple layer	0.1P Single layer
Conversion (%)	100	98.7	93	95.5
Selectivity (%)	57	55.6	53	55.7
Yield (%)	25.4	24.8	22.6	23.2

wt% contributing to enhanced olefins selectivity and reduced aromatics formation, thereby improving the nanocatalyst's performance.

Monolith coated Nanocatalyst Evaluation

The HZSM-5 and 0.1 Ge HZSM-5 nanocatalysts were further enhanced by coating them on a monolith for improved results. Monolith structured nanocatalysts were prepared using the dip coating method and evaluated at 500 °C, 1 bar pressure, and WHSV of 15 h-1. The experimental results, as shown in Table 2, indicate that there is an increase in propylene selectivity and yield with the monolith coating. Specifically, a propylene selectivity of 56.4% with 100% conversion was achieved with a single layer coating of zeolite HZSM-5 (6.8%) on the monolith. However, increasing the zeolite coating to double and triple layers resulted in a drop in methanol conversion. This drop is attributed to resistance created by product species inside the monolith channels, leading to intraparticle diffusion limitations for the reactant species.

It is important to note that radial diffusion of reacting species dominates inside the monolith nanocatalyst channels, whereas vertical axial diffusion is dominant in the nanocatalyst packed bed reactor system. The increase in propylene selectivity for the single layer monolith nanocatalyst compared to the packed bed nanocatalyst is due to better mass and heat transfer performance, lower pressure drop, and shorter contact time resulting from faster intra-diffusion rate of reactants and products inside the monolith channels.

Fig. 15 illustrates the effect of zeolite single layer, double layer, and triple layer coating on propylene selectivity and yield. Interestingly, when the single layer HZSM-5 monolith coated nanocatalyst was further modified with 0.1 wt% Germanium in hopes of improving olefins selectivity, especially propylene, the results showed a negative effect. Table 2 shows that Germanium loading led to more cracking of higher olefins in the intrapores of the zeolite nanocatalyst. Consequently, this cracking caused coke formation, resulting in rapid nanocatalyst deactivation.

In conclusion, monolith coating of the HZSM-5 nanocatalyst has demonstrated promising improvements in propylene selectivity and yield, owing to better mass and heat transfer performance and reduced pressure drop. However, the addition of Germanium as a promoter to the single-layer monolith-coated nanocatalyst did not lead to the desired effect, as it caused more cracking and deactivation of the nanocatalyst.

CONCLUSION

In this study, we investigated the selective production of propylene from methanol using monolith-structured ZSM-5 and germanium-modified ZSM-5 nanocatalysts in a fixed-bed reactor system. The optimal reaction conditions were identified as a temperature of 500 °C, a pressure of 1 bar, and a weight hourly space velocity (WHSV) of 15 h^{-1}, with methanol as the feedstock. The most effective modified nanocatalyst was achieved by incorporating 0.1 wt% germanium into ZSM-5, resulting in a significant enhancement of propylene selectivity by 53% and yield by 22.1%. Among the monolith-structured nanocatalysts, three variations were prepared: single-layer, double-layer, and triple-layer coatings of HZSM-5. The single-layer HZSM-5 monolith-coated nanocatalyst demonstrated the most substantial improvement, with propylene selectivity increasing by 55% and yield by 28.4%. These improvements were attributed to enhanced internal diffusion and reduced mass transfer resistances within the monolith channels, leading to shorter residence times and decreased aromatics formation through the decoupling of intrinsic reactions and increased olefin production. SEM images of the germanium-modified and monolith-structured HZSM-5 catalysts confirmed that there was no change in the crystallinity of the HZSM-5 catalyst. Additionally, SEM imaging revealed a uniform catalyst coating within the channels of the monolith-structured support.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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