

ผลของโพแทสเซียมเปอร์แมงกาเนตต่อตัวเร่งปฏิกิริยา CZA/13X สำหรับการสังเคราะห์แอลพีจีโดยตรง Impact of KMnO_4 on CZA/13X Catalysts for Direct LPG Synthesis

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บทคัดย่อ

การสังเคราะห์ก๊าซหุงต้ม (LPG) โดยตรงจากก๊าซสังเคราะห์ถือเป็นแนวทางที่ยั่งยืนและมีความมุ่งหวังสูงสำหรับการผลิตเชื้อเพลิงทางเลือก งานวิจัยนี้มุ่งเน้นศึกษาสมรรถนะการเร่งปฏิกิริยาของตัวเร่งปฏิกิริยาคอปเปอร์-ซิงค์-อะลูมิเนียมออกไซด์ ($\text{CuO-ZnO-Al}_2\text{O}_3$; CZA) ที่อัตราส่วนโมล 2:2:1 ซึ่งเตรียมด้วยวิธีตกตะกอนร่วมและนำมาผสมทางกายภาพกับซีโอไลต์ 13X ทั้งนี้ ได้มีการศึกษาวิจัยเป็นพิเศษเกี่ยวกับการปรับปรุงสมบัติของตัวเร่งปฏิกิริยาด้วยโพแทสเซียมเปอร์แมงกาเนต (KMnO_4) เพื่อประเมินศักยภาพในการปรับความเป็นกรดของซีโอไลต์ผ่านการส่งเสริมด้วยความเป็นด่างของโพแทสเซียม (K) และการเพิ่มการกระจายตัวของโลหะด้วยผลทางรีดอกซ์ของแมงกานีส (Mn) ระบบตัวเร่งปฏิกิริยาที่ใช้ในการประเมินมี 3 ระบบ ได้แก่ CZA/13X, CZA/10% KMnO_4 -13X และ CZA/20% KMnO_4 -13X โดยเตรียมด้วยวิธีการเคลือบฝัง KMnO_4 ลงบนซีโอไลต์ 13X ที่ความเข้มข้นร้อยละ 10 และ 20 โดยน้ำหนักต่อปริมาตร ตามลำดับ การประเมินสมรรถนะการเร่งปฏิกิริยาทดสอบภายใต้สภาวะปฏิกิริยาในเครื่องปฏิกรณ์แบบเบดนิ่ง (Fixed-bed reactor) ที่อุณหภูมิ 350 องศาเซลเซียส ความดัน 40 บาร์ และอัตราส่วนก๊าซ H_2 :CO เท่ากับ 2:1 เป็นเวลา 4 ชั่วโมง ผลการวิเคราะห์ด้วยเทคนิคก๊าซโครมาโทกราฟีพบว่าตัวเร่งปฏิกิริยา CZA/13X ที่ไม่มีการปรับปรุงให้สมรรถนะการเร่งปฏิกิริยาสูงที่สุด โดยมีค่าการเปลี่ยนก๊าซคาร์บอนมอนอกไซด์ (CO Conversion) ร้อยละ 87.64 ค่าการเลือกเกิดก๊าซ LPG (LPG Selectivity) ร้อยละ 38.16 และผลผลิตก๊าซ LPG (LPG Yield) ร้อยละ 33.47 ในขณะที่ระบบตัวเร่งปฏิกิริยาที่ปรับปรุงด้วย KMnO_4 มีสมรรถนะลดลง โดยมีค่าการเปลี่ยนก๊าซ CO ลดลงเหลือร้อยละ 86.83 และ 83.14 สำหรับปริมาณการเติมร้อยละ 10 และ 20 ตามลำดับ ผลการทดลองดังกล่าวชี้ให้เห็นว่า การดูดซับของตำแหน่งว่องไวที่เป็นกรดบนซีโอไลต์โดยสารประกอบโพแทสเซียมและแมงกานีสที่มีปริมาณมากเกินไป ส่งผลกระทบเชิงลบที่รุนแรงกว่าข้อดีที่คาดว่าจะได้รับการส่งเสริมทางรีดอกซ์หรือความเป็นด่าง จึงเป็นการขัดขวางขั้นตอนการเปลี่ยนเมทานอลไปเป็นไฮโดรคาร์บอน (Methanol-to-hydrocarbon dehydration step) ข้อค้นพบเหล่านี้เน้นย้ำถึงความสำคัญของความสมดุลระหว่างฟังก์ชันโลหะและฟังก์ชันกรด และบ่งชี้ว่าแม้การปรับปรุงด้วย KMnO_4 จะถูกคาดหวังเพื่อใช้ในการควบคุมค่าการเลือกเกิดผลิตภัณฑ์ แต่ในสภาวะที่ทำการศึกษานี้กลับให้ผลในทางตรงกันข้ามเนื่องจากการเข้ายั่วยุตำแหน่งว่องไวหลักของตัวเร่งปฏิกิริยา

คำสำคัญ: การสังเคราะห์แอลพีจี, ตัวเร่งปฏิกิริยาสองฟังก์ชัน, การดัดแปลงด้วย KMnO_4 , ตัวเร่งปฏิกิริยาคอปเปอร์-ซิงค์-อะลูมิเนียม

Abstract

The direct synthesis of liquefied petroleum gas (LPG) from synthesis gas represents a promising sustainable pathway for alternative fuel production. This study investigates the catalytic performance of copper-zinc-aluminum oxide catalysts ($\text{CuO-ZnO-Al}_2\text{O}_3$; CZA) with molar ratio 2:2:1, prepared via a co-precipitation method and physically mixed with zeolite 13X. The modification using KMnO_4 was specifically explored to evaluate its potential in tuning zeolite acidity through alkali (K) promotion and enhancing metal dispersion via manganese (Mn) redox effects. Three catalyst systems were evaluated: CZA/13X, CZA/10% KMnO_4 -13X, and CZA/20% KMnO_4 -13X, where potassium permanganate was impregnated onto zeolite 13X at concentrations of 10% and 20% w/v respectively. Catalytic performance was assessed using a fixed-bed reactor at 350°C, 40 bar, with H_2 :CO ratio of 2:1 for 4 h. Gas chromatography analysis revealed that unmodified CZA/13X exhibited the highest catalytic activity with a CO conversion of 87.64%, LPG selectivity of 38.16%, and LPG yield of 33.47%. In comparison, the KMnO_4 -modified systems showed decreased performance, with CO conversions of 86.83% and 83.14% for the 10% and 20% loading, respectively. These results suggest that the excessive blockage of zeolite acid sites by potassium and manganese species outweighs any potential benefits from redox or basic promotion, thereby hindering the methanol-to-hydrocarbon dehydration step. These findings highlight the critical balance of the metal-acid functions and indicate that while KMnO_4 modification was expected to tune selectivity, it proved counterproductive under the studied conditions due to the suppression of key active sites.

Keywords: LPG synthesis, Bifunctional catalyst, KMnO_4 modification, Copper-zinc-aluminum catalyst

1. Introduction

The global energy paradigm is currently undergoing an unprecedented transition, catalyzed by the surging demand for sustainable energy alternatives, the depletion of conventional hydrocarbon reserves, and the critical need to mitigate greenhouse gas emissions (Chu & Majumdar, 2012; Gielen et al., 2019). In this shifting landscape, Liquefied Petroleum Gas (LPG), primarily a blend of propane (C_3H_8) and butane (C_4H_{10}), has gained significant recognition as a strategic transitional fuel. Its high energy density, versatile applications across residential and industrial sectors, and relatively low emission profile render it a superior alternative to traditional solid and liquid fuels (Raslavičius et al., 2014). In the context of Thailand, LPG is integral to the domestic energy framework, serving as a primary fuel source for households and the transportation sector. Within the strategic framework of the Bio-Circular-Green (BCG) Economy and the national Alternative Energy Development Plan (AEDP), there is an intensifying focus on enhancing energy self-sufficiency. Consequently, the development of advanced technologies for the direct synthesis of LPG from indigenous carbon sources such as agricultural waste or biogas represents a critical step toward reducing reliance on energy imports and achieving carbon neutrality.

Traditionally, LPG production is tethered to petroleum refining and natural gas processing; however, the inherent volatility of crude oil markets and the diminishing accessibility of fossil reserves present

significant risks to energy security (Apergis & Miller, 2009). To address these challenges, the direct synthesis of LPG from syngas ($\text{CO} + \text{H}_2$) has emerged as a promising thermo-chemical pathway. This process allows for the utilization of diverse feedstocks, including biomass-derived syngas and captured CO_2 , thereby aligning with circular economy principles and providing a sustainable route for fuel production (Palgunadi et al., 2010).

The Fischer-Tropsch (FT) process, discovered in the 1920s, converts syngas to liquid hydrocarbons through surface polymerization reactions over metal catalysts. While conventional FT synthesis typically targets longer-chain hydrocarbons, modified approaches can be tailored for LPG production (Mahmoudi et al., 2017). Recent studies have demonstrated that bifunctional catalyst systems combining methanol synthesis functionality with acid catalysis can achieve direct conversion of CO and H_2 to LPG through a modified methanol-to-hydrocarbons pathway (Weber et al., 2024). Research by Tavares et al. (2022) showed that Cu-Zn-Al catalysts modified with various zeolites could achieve CO conversions exceeding 80% with significant LPG selectivity. Similarly, Ramirez et al. (2019) demonstrated that the acid strength and pore structure of zeolite supports critically influence product distribution in syngas conversion processes. To further optimize this system, the introduction of promoters such as manganese (Mn) and potassium (K) has been explored. Manganese is known to act as a redox promoter that enhances Cu dispersion and CO adsorption, which can significantly improve catalytic activity (Palgunadi et al., 2010). Concurrently, the use of KMnO_4 as a precursor provides inherent alkalinity from potassium (K), which serves as an electronic modifier to tune the surface acidity of the zeolite. This modification is crucial for neutralizing overly strong acid sites that otherwise lead to excessive cracking and methane formation, thereby shifting the selectivity towards the desired $\text{C}_3\text{-C}_4$ range (Ao et al., 2020). Furthermore, manganese oxides can act as structural stabilizers, preventing the sintering of active metal phases under high-temperature reaction conditions (Beerthuis et al., 2021).

The direct synthesis of LPG from syngas involves a complex reaction network that can be simplified into key sequential steps:

Primary methanol synthesis reaction:



Methanol dehydration to dimethyl ether:



DME and methanol conversion to hydrocarbons:



Water-gas-shift side reaction:



The overall process is thermodynamically favored and exothermic, with an approximate enthalpy change of -210 kJ/mol. The methanol synthesis step (Equation 1) is catalyzed by the Cu-Zn-Al component and is thermodynamically limited by equilibrium. Subsequently, methanol undergoes acid-catalyzed dehydration and oligomerization reactions on zeolite acid sites to form longer-chain hydrocarbons including LPG components (Equations 2-4). The water-gas-shift reaction (Equation 5) represents a significant side reaction that can influence overall carbon efficiency (Ma et al., 2015; Xiangang et al., 2011). Recent mechanistic studies using in-situ spectroscopic techniques have revealed that the balance between metal and acid functions is crucial for optimizing LPG selectivity while minimizing undesired products such as methane and higher hydrocarbons (Liu et al., 2018). The proximity and interaction between Cu-based methanol synthesis sites and zeolite acid sites significantly impact intermediate species diffusion and subsequent conversion pathways.

The conceptual framework of this research is built upon the synergy between the CZA metallic function and the modified 13X zeolite acid function, where the KMnO_4 loading serves as a critical independent variable to balance these two pathways. This study aims to systematically evaluate the catalytic performance of $\text{CuO-ZnO-Al}_2\text{O}_3/13\text{X}$ zeolite bifunctional catalysts for direct LPG synthesis from syngas, with particular focus on understanding the effects of KMnO_4 modification on zeolite 13X support. While previous studies have explored various metal oxide promoters, the specific role of manganese oxide species in modulating acid-base properties and their impact on LPG selectivity remains understudied.

The key objectives of this work include: (1) systematic comparison of unmodified versus KMnO_4 -modified 13X zeolite supports, (2) evaluation of physical mixing ratios between methanol synthesis and acid catalysis components, and (3) comprehensive characterization linking catalyst structure to performance for direct LPG synthesis applications.

2. Materials and Methods

2.1 Catalyst Preparation

2.1.1 Co-Precipitation of $\text{CuO-ZnO-Al}_2\text{O}_3$ (CZA)

The $\text{CuO-ZnO-Al}_2\text{O}_3$ catalyst was synthesized via a co-precipitation method following optimized procedures from literature (Janjira & Promarin, 2022). Aqueous solutions of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Sigma-Aldrich, 99% purity) were prepared to achieve a $\text{CuO:ZnO:Al}_2\text{O}_3$ molar ratio of 2:2:1. The mixed metal nitrate solution (total metal concentration: 2.0 M) was added dropwise to 500 mL of Na_2CO_3 solution (0.05 M) under continuous stirring (600 rpm) while maintaining pH at 7.0 ± 0.1 and temperature at 70 °C using an automated pH control system.

After complete precipitation, the suspension was aged for 24 h at room temperature, followed by washing with deionized water (80 °C) until nitrate-free (confirmed by AgNO_3 test). The precipitate was dried at 80 °C for 12 h and calcined at 350 °C for 5 h with a heating rate of 2°C/min under air atmosphere.

2.1.2 Zeolite 13X Preparation and Modification

Commercial grade NaX zeolite (Zeochem, Si/Al = 1.2) was used as received. Prior to use, the zeolite was thermally treated at 110 °C for 3 hours to remove physisorbed water, followed by calcination at 350 °C for 5 h to ensure complete activation.

For KMnO₄ modification, incipient wetness impregnation was employed. KMnO₄ solutions with concentrations of 10% and 20% w/v were prepared using deionized water. The calculated amount of KMnO₄ solution was slowly added to pre-dried zeolite 13X (3.5 g KMnO₄ in 35 mL water for 10% loading; 7.0 g KMnO₄ in 35 mL water for 20% loading) until complete absorption. The impregnated materials were stirred for 1 h, dried at 110 °C for 12 h, and finally calcined at 350 °C for 5 h to decompose KMnO₄ into MnO₂ and K₂O species.

2.1.3 Catalyst Pelletization and Physical Mixing

All catalyst components were pelletized using a hydraulic press at 3000 psi and sieved to 850 μm particle size to ensure uniform flow characteristics in the fixed-bed reactor. Bifunctional catalysts were prepared by physical mixing of 0.33 g CZA with 0.17 g of acid catalyst (13X, 10% KMnO₄-13X, or 20% KMnO₄-13X) to achieve a 2:1 mass ratio, along with 0.5 g quartz sand as a diluent to minimize hot spot formation.

2.2 Catalyst Characterization

2.2.1 Structural Characterization

X-ray diffraction (XRD) patterns were recorded using a Rigaku Mini Flex diffractometer with Cu Kα-radiation ($\lambda = 1.5418 \text{ \AA}$) operating at 40 kV and 15 mA. Scans were performed over a 2θ range of 10–90° with a step size of 0.02° and counting time of 2 s per step. Phase identification was accomplished using the JCPDS database, and crystallite sizes were calculated using the Scherrer equation:

$$d_{\text{crystallite}} = \frac{K\lambda}{\beta \cos\theta} \quad (6)$$

Where K is the Scherrer constant (0.94 for spherical crystals with cubic symmetry) and λ represents the wavelength of the incident radiation. β is the full width at half maximum (FWHM) and θ is the position of the diffraction peak. The surface area of the reduced copper particles (S_{Cu} , in $\text{m}_{\text{Cu}}^2\text{-g}_{\text{Cat}}^{-1}$) was calculated using equation (7), where ρ_{Cu} is 8.93 g-cm^{-3} (density of copper), and W is the mass fraction of copper in the catalyst (Nanchaphak, 2021; Laksika & Runarat, 2020).

$$S_{\text{Cu}} = \frac{6000 \times W}{\rho_{\text{Cu}}} d_{\text{Cu}} \quad (7)$$

2.2.2 Surface Properties and Acidity Analysis

Brunauer-Emmett-Teller (BET) surface area, pore volume, and pore size distribution were determined using N₂ physisorption at -196 °C (Micromeritics ASAP 2020). Samples were degassed at 350 °C for 4 h prior to analysis.

Acid site concentration and strength distribution were characterized using temperature-programmed desorption of ammonia (NH₃-TPD) on a Micromeritics AutoChem II 2920 analyzer. Samples (100 mg) were pretreated at 350 °C under He flow, cooled to 100°C, and saturated with 10% NH₃/He. After purging with He, TPD was conducted from 100-800 °C at 10°C/min a heating rate while monitoring NH₃ desorption by thermal conductivity detector.

2.3 Catalytic Performance Evaluation

Catalytic testing was performed in a fixed-bed stainless steel reactor (inner diameter: 10 mm; length: 300 mm) equipped with temperature and pressure control systems. The catalyst activation protocol consisted of: (1) purging with N₂ at 150 °C for 24 min, (2) reduction with 5% H₂/N₂ at 250 °C for 2 h, and (3) final temperature adjustment to reaction conditions.

Reaction conditions were optimized based on literature recommendations: 350 °C, 40 bar, H₂:CO = 2:1, a total flow rate of 20 mL/min (STP), and a reaction time of 4 h. Product analysis was performed using online Gas Chromatography. Permanent gases (H₂, CO, CO₂, and N₂) were quantified using a Thermal Conductivity Detector (TCD), while hydrocarbons (C₁-C₅) were analyzed via a Flame Ionization Detector (FID) using appropriate capillary columns.

The catalytic performance metrics, including CO conversion, LPG selectivity, and LPG yield, were calculated based on the carbon mole balance as follows:

$$\text{CO Conversion (\%X}_{\text{CO}}) = (\text{nCO}_{\text{in}} - \text{nCO}_{\text{out}}) / \text{nCO}_{\text{in}} \times 100$$

where nCO_{in} and nCO_{out} are the molar flow rates of CO at the inlet and outlet, respectively.

$$\text{LPG Selectivity (\%S}_{\text{LPG}}) = \sum(i \cdot \text{nC}_{i,\text{out}}) / \sum(j \cdot \text{nC}_{j,\text{out}}) \times 100$$

where i represents carbon numbers in the LPG range (C₃ and C₄), j represents all carbon-containing products except CO₂ (unless specified), and nC is the molar flow rate of the respective hydrocarbon product.

$$\text{LPG Yield (\%Y}_{\text{LPG}}) = \text{X}_{\text{CO}} \times \text{S}_{\text{LPG}} / 100$$

3. Results

3.1 Catalyst Characterization Results

3.1.1 XRD Analysis and Phase Composition

The X-ray diffraction (XRD) patterns of the prepared catalysts are presented in Figure 1, which clearly demonstrates the crystalline phases present in each catalyst system and provides crucial insights into the structural properties of the bifunctional catalysts. The diffraction analysis confirms the successful formation of all expected phases and reveals important information about crystallite sizes and phase interactions. For the CZA/13X catalyst system, the XRD pattern shows characteristic peaks for each component. The CuO phase, which serves as the primary active component for methanol synthesis, exhibited sharp and intense peaks at $2\theta = 35.90^\circ$, 62.34° , and 68.16° corresponding to the (111), (113), and (220) crystal planes respectively. These peaks indicate a well-crystallized monoclinic CuO structure, which is essential for catalytic activity. The peak intensities suggest good dispersion of copper oxide throughout the catalyst matrix.

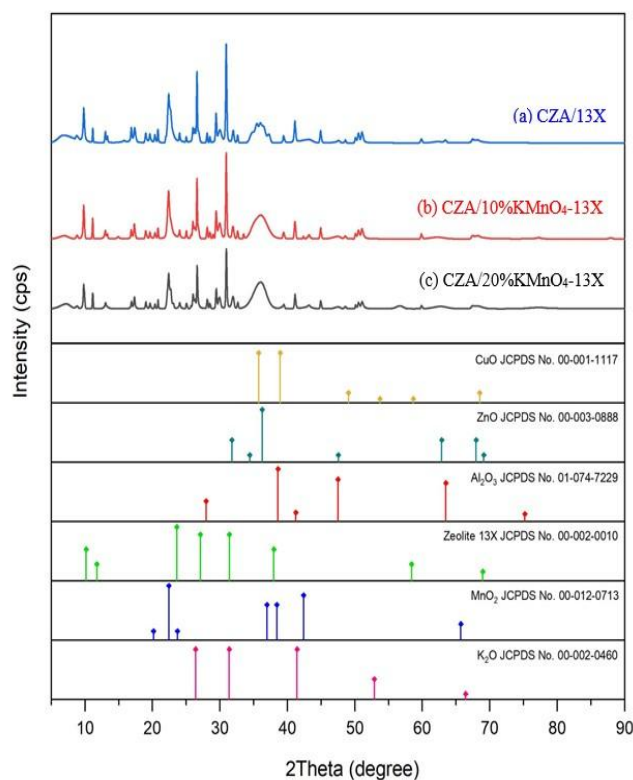


Figure 1. XRD patterns of the metal oxide catalysts showing phase identification for (a) CZA/13X, (b) CZA/10%KMnO₄-13X, and (c) CZA/20%KMnO₄-13X with corresponding reference peak positions.

The ZnO component, acting as a structural and electronic promoter for the copper phase, showed characteristic reflections at $2\theta = 31.91^\circ$, 34.74° , and 36.39° corresponding to the (100), (002), and (101) planes of the hexagonal wurtzite structure. The presence of these peaks confirms that zinc oxide maintains its crystalline integrity during the co-precipitation and calcination processes. The relatively high intensity of the (002) peak suggests preferred orientation along the c-axis, which is known to influence the promotional effect on copper catalysts.

Al₂O₃ exhibited typical γ -alumina reflections at $2\theta = 28.07^\circ$, 50.51° , and 67.41° for the (012), (202), and (122) planes respectively. The broad nature of these peaks is characteristic of the poorly crystalline γ -Al₂O₃ phase, which provides structural stability and prevents sintering of the active copper and zinc oxide phases under reaction conditions. The presence of γ -alumina is particularly important for maintaining catalyst stability during long-term operation.

The 13X zeolite framework was confirmed by its characteristic diffraction pattern with peaks at $2\theta = 10.16^\circ$, 11.74° , 23.60° , 27.11° , and 31.40° . These peaks correspond to the faujasite structure with its three-dimensional pore system, which is crucial for the acid-catalyzed conversion of methanol to hydrocarbons. The sharpness of these peaks indicates that the zeolite structure remains intact throughout the catalyst preparation process, preserving its microporous properties and acid site accessibility.

The KMnO₄-modified catalysts displayed additional diffraction features that provide important insights into the modification effects. Both 10% and 20% KMnO₄-modified systems showed new peaks

corresponding to MnO_2 at $2\theta = 20.34^\circ$, 22.36° , 43.16° , and 67.87° , which correspond to the (110), (101), (211), and (301) reflections of $\beta\text{-MnO}_2$ (pyrolusite structure). The intensity of these peaks increased proportionally with KMnO_4 loading, confirming quantitative decomposition of the permanganate precursor during calcination. The formation of $\beta\text{-MnO}_2$ rather than other manganese oxide phases is significant because this polymorph typically exhibits different catalytic and electronic properties.

Additionally, the modified catalysts showed reflections characteristic of K_2O at $2\theta = 29.58^\circ$, 41.13° , and 44.93° , corresponding to the (111), (200), and (220) planes of the cubic potassium oxide structure. The presence of these peaks confirms that potassium species are not merely dispersed on the surface but form distinct crystalline domains. This crystalline K_2O may contribute to changes in the catalyst's basicity and electronic properties.

Quantitative analysis using the Scherrer equation provided valuable information about crystallite sizes and dispersion characteristics. The calculated data are summarized in Table 1, which shows that the CuO crystallite size in the CZA component is 12.25 nm, corresponding to a metallic copper particle size of 9.19 nm after reduction. This results in a copper dispersion of 10.45%, which is within the optimal range for methanol synthesis activity.

The results presented in Table 1 reveal that the CuO crystallite size obtained in this study (12.25 nm) is larger than previously reported values (6.30 nm), which may be attributed to differences in synthesis conditions, particularly calcination temperature and time, or variations in precipitation pH. The larger crystallite size results in lower copper dispersion (10.45% vs 20.32%), but this value remains within the range considered suitable for methanol synthesis applications. The moderate dispersion may actually be beneficial for stability, as highly dispersed copper particles are more susceptible to sintering under reaction conditions.

Table 1. Particle diameters and copper surface areas of the different catalysts.

Catalysts	d (CuO)	d (Cu^0)	Dispersion (%)	Reference
CZA (2:2:1)	12.25	9.19	10.45	This study
CZA (2:2:1)	6.30	4.73	20.32	Nanchaphak (2021)

The peak broadening analysis also revealed that KMnO_4 modification does not significantly affect the crystallite sizes of the primary CZA components, suggesting that the impregnation process does not cause substantial structural changes to the methanol synthesis catalyst. However, the presence of MnO_2 and K_2O phases may influence the local electronic environment and affect the reducibility and catalytic properties of the copper phase.

3.1.2 Surface Morphology and Composition

SEM analysis provided comprehensive insights into the morphological characteristics and spatial distribution of components in each catalyst system. The morphological investigation is crucial for

understanding how the physical mixing process affects catalyst performance and provides evidence for the successful integration of methanol synthesis and acid catalysis functionalities.

Energy dispersive X-ray spectroscopy (EDS) results are presented in Figure 2, which confirms the elemental composition of all three catalyst systems and validates the theoretical stoichiometry. The EDS analysis demonstrates that the co-precipitation method successfully produced the intended 2:2:1 molar ratio of $\text{CuO}:\text{ZnO}:\text{Al}_2\text{O}_3$, with measured compositions closely matching the intended theoretical stoichiometry. The mapping of elemental signals showed a uniform distribution of copper (Cu), zinc (Zn), and aluminum (Al) across the analyzed microscopic regions. For the modified catalysts, the EDS results further validated the presence of manganese and potassium, consistent with the added KMnO_4 loadings.

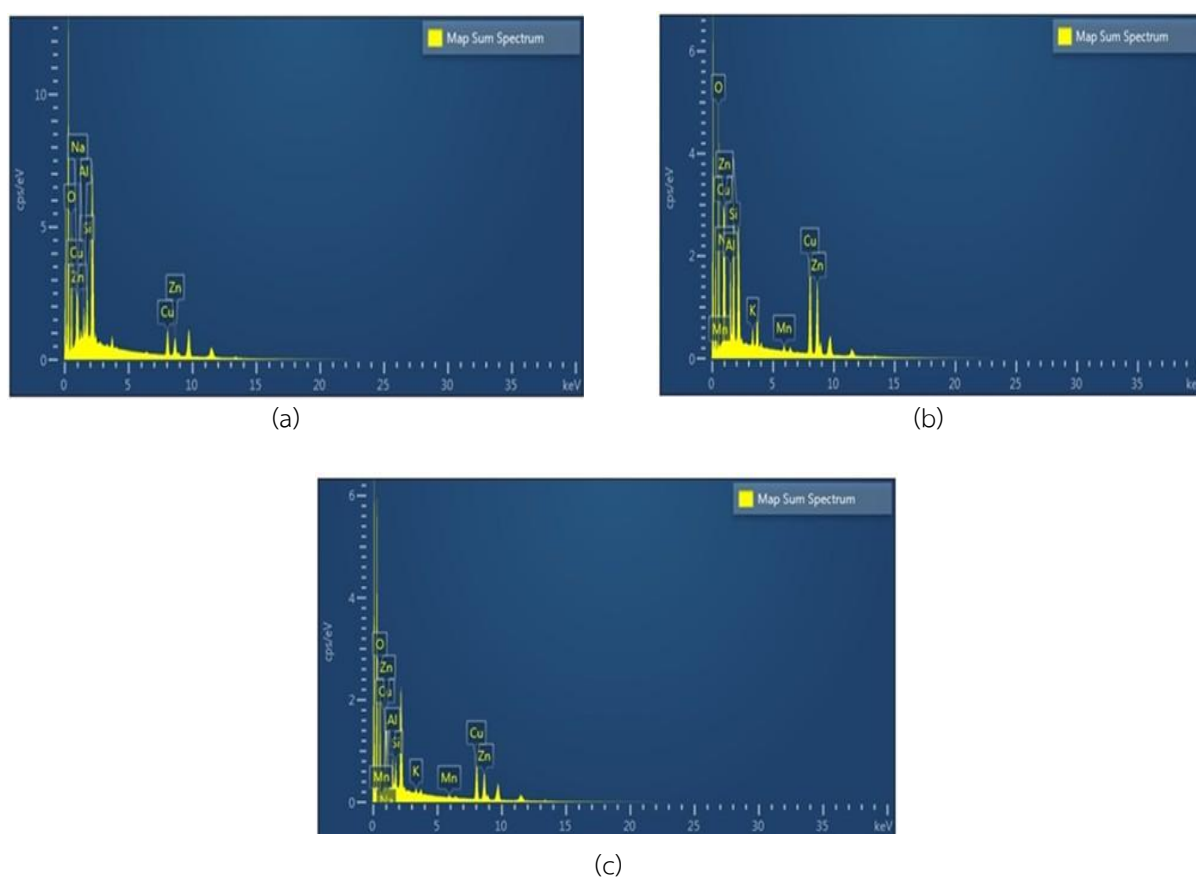


Figure 2. EDS spectra of (a) CZA/13X, (b) CZA/10%KMnO₄-13X and (c) CZA/20%KMnO₄-13X, catalysts showing elemental composition validation.

3.1.3 Surface area and Porosity (BET) Analysis

For the modified catalysts, EDS analysis clearly detected manganese and potassium peaks, confirming successful impregnation of KMnO_4 and its subsequent decomposition to MnO_2 and K_2O during calcination. The intensity of manganese signals increased proportionally with loading levels, validating the quantitative nature of the impregnation process.

The morphological characteristics are detailed in the SEM micrographs, which provide multi-scale visualization of catalyst architecture from macro-aggregates to surface details. Figure 3 presents the CZA/13X catalyst morphology at various magnifications, revealing particle aggregates ranging from 10–50 μm in diameter, which is suitable for fixed-bed reactor applications as it minimizes pressure drop while maintaining good mass transfer characteristics according to Mahmoudi et al. (2017).

At higher magnifications (10,000–40,000 $\times$), the distinct morphological characteristics of each component become apparent. The CZA particles exhibit rough, cauliflower-like surfaces with high surface roughness, which is typical of co-precipitated metal oxide catalysts and beneficial for providing high surface area for methanol synthesis reactions (Tavares et al., 2022). The interface between CZA and zeolite particles is of particular importance for bifunctional catalysis, as emphasized by Liu et al. (2018) in their mechanistic studies using in-situ spectroscopic techniques.

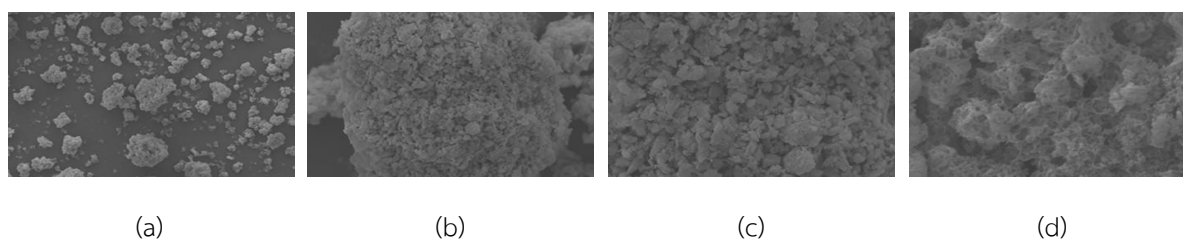


Figure 3. SEM micrographs of CZA/13X catalysts at magnifications of (a) 1,500 $\times$, (b) 10,000 $\times$, (c) 20,000 $\times$, and (d) 40,000 $\times$, showing the physical mixing of CZA particles with 13X zeolite crystals.

Figure 4 shows the morphology of CZA/10%KMnO₄-13X catalysts, where the effects of permanganate impregnation become clearly visible. The rod-shaped and needle-like MnO₂ structures observed are characteristic of β -MnO₂ formation during thermal decomposition, as documented by Weber et al. (2024) in their studies of manganese oxide phase transformations.

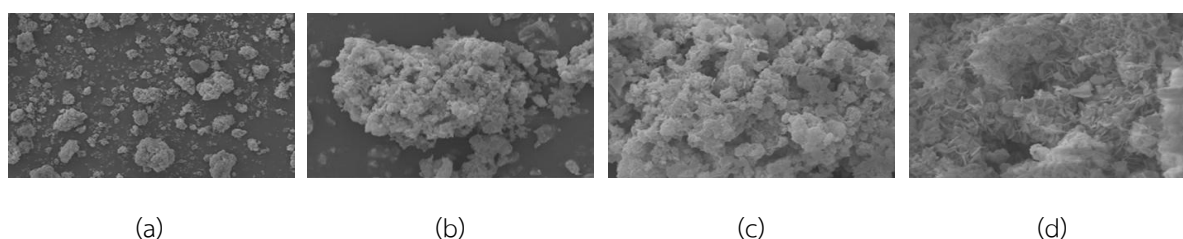


Figure 4. SEM micrographs of CZA/10%KMnO₄-13X catalysts at magnifications of (a) 1,500 $\times$, (b) 10,000 $\times$, (c) 20,000 $\times$, and (d) 40,000 $\times$, displaying rod-shaped MnO₂ aggregates on zeolite surfaces.

The preferential deposition pattern observed near zeolite pore openings and crystal edges suggests that the impregnation process is controlled by capillary forces and surface energy

considerations, which align with the theoretical framework proposed by Ramirez et al. (2019) for understanding metal oxide distribution in zeolite supports.

The progressive blocking of zeolite pores observed at higher loadings correlates well with studies by Argyle & Bartholomew (2015) on catalyst deactivation mechanisms, where pore blockage was identified as a primary cause of reduced activity in modified zeolite catalysts.

The textural properties of the catalysts, as determined by nitrogen physisorption and BET analysis, provide critical insights into the effects of KMnO_4 modification on the porous structure of the zeolite support and its implications for catalytic performance. The comprehensive data presented in Table 2 reveal significant differences in surface area, pore volume, and pore size distribution among the catalyst systems, which directly correlate with the observed catalytic behavior.

The pristine CZA component exhibits a moderate surface area of $174.45 \text{ m}^2/\text{g}$ with a relatively large average pore size of $128.10 \text{ \AA}$, which is characteristic of co-precipitated metal oxide catalysts. This pore structure is predominantly mesoporous, resulting from the aggregation of small oxide crystallites during the co-precipitation and calcination processes. The large pore size facilitates reactant and product diffusion, which is particularly important for preventing mass-transfer limitations during methanol synthesis from syngas. The pore volume of $0.58 \text{ cm}^3/\text{g}$ indicates a well-developed porous structure that provides adequate space for gas-phase reactions.

Table 2. Surface area and porosity analysis of catalyst components.

Catalysts	Surface area (m^2/g)	Pore volume (cm^3/g)	Pore size ($\text{\AA}$)	Reference
CZA	174.45	0.58	128.10	Praphaporn & Satawat (2021)
13X	637.91	0.51	32.09	Thanaporn & Pisek (2021)
10% KMnO_4 -13X	495.92	0.39	31.34	Thanaporn & Pisek (2021)
20% KMnO_4 -13X	313.89	0.27	34.62	Thanaporn & Pisek (2021)

In contrast, the pristine 13X zeolite displays a significantly higher surface area of $637.91 \text{ m}^2/\text{g}$, which is typical for Faujasite-type zeolites with their three-dimensional microporous framework. The average pore size of $32.09 \text{ \AA}$ corresponds to the supercage dimensions of the faujasite structure, where the main catalytic reactions involving acid sites occur. The pore volume of $0.51 \text{ cm}^3/\text{g}$ reflects the high micropore volume characteristic of 13X zeolite, which is essential for providing a large number of accessible acid sites for methanol dehydration and subsequent oligomerization reactions.

The effects of KMnO_4 impregnation on the textural properties are clearly evident from the data in Table 2. The 10% KMnO_4 -13X sample shows a substantial decrease in surface area to $495.92 \text{ m}^2/\text{g}$, representing a 22% reduction compared to the pristine zeolite. This decrease is accompanied by a reduction in pore volume from 0.51 to $0.39 \text{ cm}^3/\text{g}$ (24% decreased), while the average pore size remains relatively unchanged at $31.34 \text{ \AA}$. These changes indicate that the MnO_2 and K_2O deposits formed during

KMnO₄ decomposition partially block the zeolite pores without significantly altering the remaining accessible pore dimensions.

Figure 5 shows that the morphology of CZA/20%KMnO₄-13X sample exhibits even more pronounced textural changes, with the surface area dropping dramatically to 313.89 m²/g (51% reduction) and pore volume decreasing to 0.27 cm³/g (47% reduction). The average pore size increases slightly to 34.62 Å, suggesting that smaller pores are preferentially blocked while larger pores remain accessible. This pore size distribution shift indicates that the impregnation process affects pores of different sizes to varying degrees.

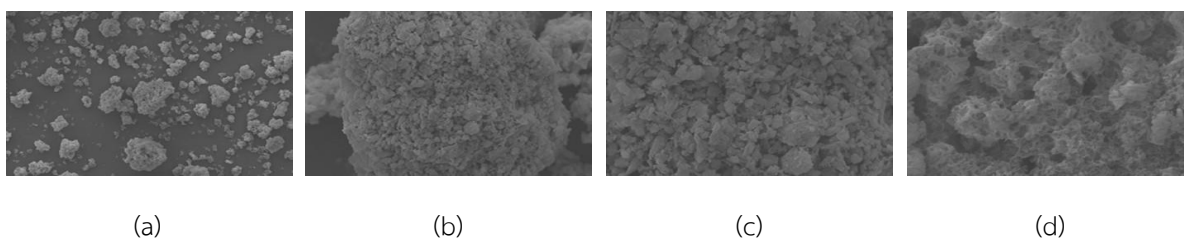


Figure 5. SEM micrographs of CZA/20%KMnO₄-13X catalysts at magnifications of (a) 1,500X, (b) 10,000X, (c) 20,000X, and (d) 40,000X, showing increased density of MnO₂ deposits due to higher KMnO₄ loading.

3.1.4 Acidity Characterization

The acid site properties of the 13X zeolite were characterized using NH₃-TPD analysis, as shown in Figure 6. The desorption profile exhibits a complex pattern with multiple overlapping peaks, which can be deconvoluted into two primary regions based on temperature (David & Armeanu, 2022).

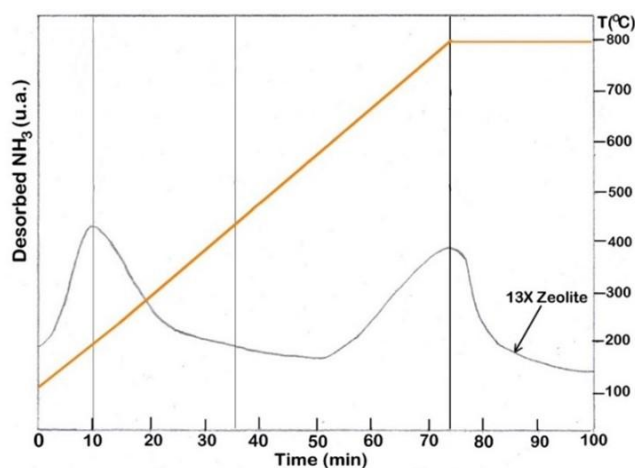


Figure 6. NH₃-TPD analysis results of 13X zeolite showing temperature-programmed desorption profile with weak and strong acid site distributions (David & Armeanu, 2022).

The low-temperature desorption peak, centered around 125°C, corresponds to ammonia molecules weakly bound to Brønsted acid sites or physisorbed on the zeolite surface. These sites typically exhibit acid strength in the range of 26-35 $\mu\text{mol/g}$ and are associated with silanol groups or weakly acidic bridging hydroxyl groups located primarily on the external surface or in the larger cavities of the zeolite structure. While these weak acid sites contribute to the total acidity, they are generally not sufficient alone to catalyze the dehydration and oligomerization reactions required for LPG formation.

The high-temperature desorption region, with a broad peak extending from 300 °C to approximately 500 °C and centered around 400°C, represents ammonia desorbing from strong Brønsted acid sites. These sites are primarily associated with bridging hydroxyl groups (Si-OH-Al) located within the zeolite framework, particularly in the sodalite cages and hexagonal prisms of the faujasite structure. The total concentration of these strong acid sites ranges from 62-750 $\mu\text{mol/g}$, representing the primary catalytically active centers for methanol dehydration and subsequent hydrocarbon formation reactions.

The analysis also reveals that substantial ammonia desorption occurs only at temperatures surpassing 300°C, providing data on the thermal stability of these sites under the research reaction temperature of 350°C.

3.2 Catalytic Performance Evaluation

3.2.1 CO Conversion Analysis

The catalytic activity results provide evidence for the different performance of the unmodified CZA/13X system compared to the KMnO_4 -modified alternatives, with CO conversion serving as a primary indicator of overall catalyst effectiveness. The CO conversion data, presented in Figure 7, demonstrate clear performance differences among the catalyst systems and reveal important insights into the effects of zeolite modification on syngas conversion activity.

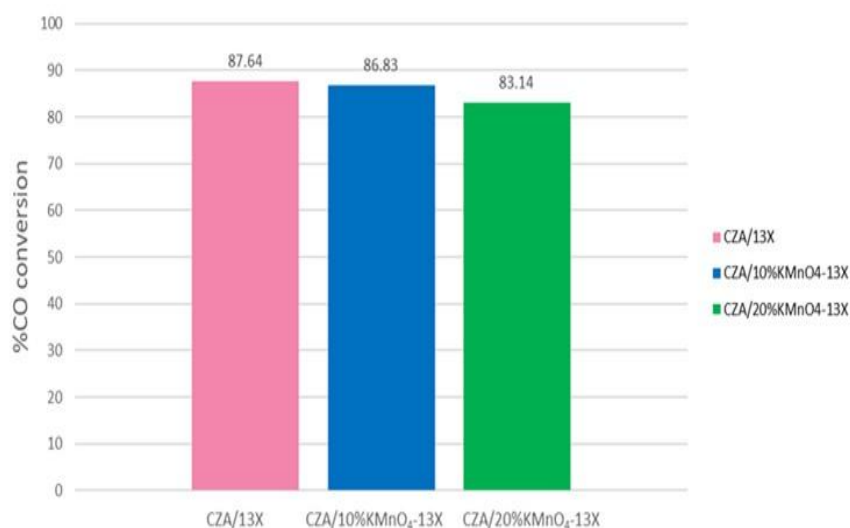


Figure 7. %CO conversion of different catalyst systems showing superior performance of unmodified CZA/13X catalyst.

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3.2.2 Product Selectivity and Distribution

The product selectivity results provide crucial insights into how catalyst composition affects the distribution of products formed during syngas conversion, with particular emphasis on the formation of desired LPG components versus other hydrocarbons and byproducts. The LPG selectivity data, illustrated in Figure 8, reveal striking and unexpected differences among the catalysts that highlight the importance of maintaining unobstructed access to acid sites.

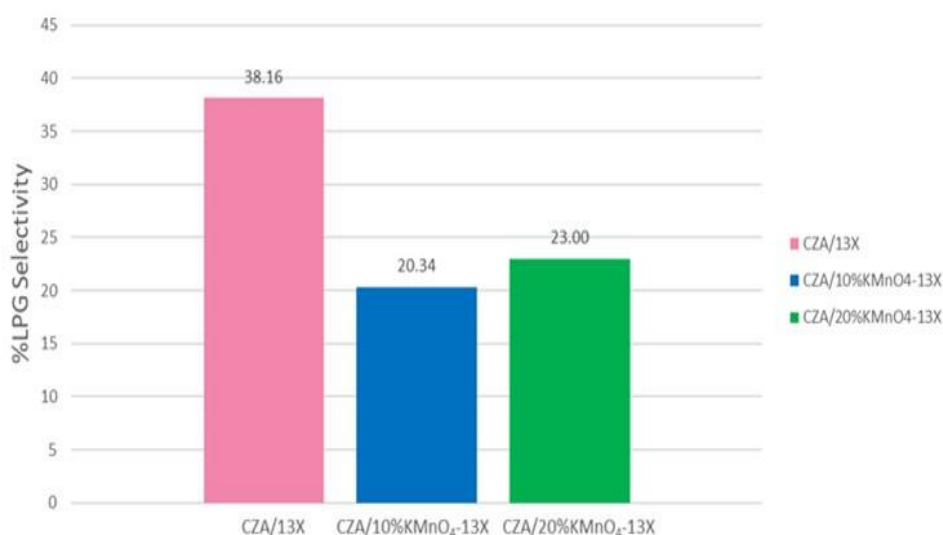


Figure 8. LPG selectivity (%) of different catalyst systems demonstrating the advantage of unmodified zeolite support.

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reveal striking and unexpected differences among the catalysts that highlight the importance of maintaining unobstructed access to acid sites. The most notable finding is the substantially higher LPG selectivity achieved by the unmodified CZA/13X system (38.16%) compared to both modified catalysts: CZA/20%KMnO₄-13X (23.00%) and CZA/10%KMnO₄-13X (20.34%).

3.2.3 Overall LPG Yield Performance

The LPG yield results represent the most practically important performance metric as they combine both conversion and selectivity effects to provide a comprehensive measure of catalyst effectiveness for the intended application. The yield data, presented in Figure 9, demonstrate the higher performance of the unmodified CZA/13X system and provide quantitative evidence for the negative effects of KMnO₄ modification.

The LPG yield results represent the most practically important performance metric as they combine both conversion and selectivity effects to provide a comprehensive measure of catalyst effectiveness for the intended application. The yield data demonstrate the superior performance of the unmodified CZA/13X system and provide quantitative evidence for the negative effects of KMnO₄ modification. The CZA/13X catalyst achieved the highest LPG yield of 33.47%, while the modified catalysts showed significantly lower yields: 17.66% for CZA/10%KMnO₄-13X and 19.12% for CZA/20%KMnO₄-13X.

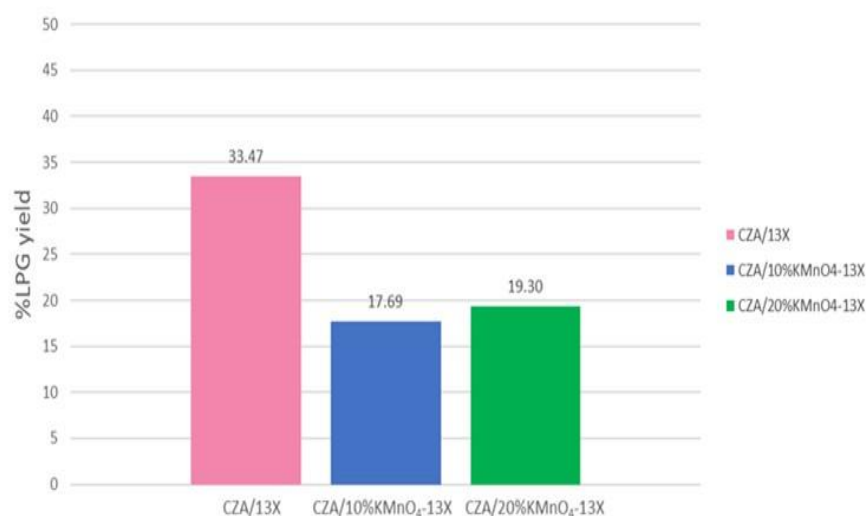


Figure 9. LPG yield (%) for different catalyst systems, showing the superior performance of the unmodified CZA/13X bifunctional catalyst.

The data presented in Table 3 reveal several important trends that provide insights into the underlying causes of performance differences, consistent with structure-activity relationships established by Tavares et al. (2022) in their systematic catalyst optimization studies. First, the decline in CO conversion with increasing KMnO₄ loading follows a clear trend, suggesting that the negative effects of

modification are cumulative and become more severe at higher loadings, which aligns with threshold behavior models proposed by Liu et al. (2018).

Table 3. Carbon monoxide conversion (%), product selectivity (%), and LPG yield (%).

Catalysts	CO conversion (%)	LPG selectivity (%)	HC Selectivity (%)	DME selectivity (%)	LPG yield (%)
CZA/13X	87.64	38.16	99.92	0.14	33.47
CZA/10%KMnO ₄ -13X	89.83	20.34	99.90	0.13	17.69
CZA/20%KMnO ₄ -13X	83.14	23.00	99.99	0.01	19.30

Second, the LPG selectivity shows an even more dramatic decline than CO conversion, indicating that the modification affects product distribution more severely than overall activity. This finding suggests that the modification disrupts the delicate balance of reaction conditions required for selective LPG formation, possibly through changes in acid site distribution or the introduction of competing reaction pathways, as demonstrated by Weber et al. (2024) in their mechanistic studies of modified zeolite catalysts.

The yield data provide significant insights into the economic viability of catalyst selection for industrial-scale operations. The substantially higher yields achieved by the unmodified system directly correlate with enhanced product recovery rates, which is a primary driver for optimizing process economics. Furthermore, the streamlined preparation protocol for the unmodified catalyst offers a distinct advantage by eliminating the additional impregnation and drying steps required for modification. This reduction in synthesis complexity not only lowers manufacturing costs but also minimizes the potential for batch-to-batch variability, representing a significant economic and operational benefit as identified by Ramirez et al. (2019) in their process optimization studies.

3.3 Structure-Performance Relationships

The experimental data reveal a strong correlation between the structural integrity of the catalysts and their catalytic performance. The unmodified CZA/13X system, characterized by unobstructed 13X zeolite supercages and moderate Brønsted acidity, consistently yielded the highest LPG selectivity (38.16%). In contrast, the KMnO₄-modified catalysts exhibited progressive pore blockage and a reduction in acid site density as the loading of MnO₂ and K₂O increased. SEM and BET data confirm that these deposits are non-uniformly distributed, creating a heterogeneous surface that corresponds with the cumulative decline in CO conversion and LPG yield observed in the performance tests.

4. Discussion

4.1 Catalyst Characterization Results

4.1.1 XRD Analysis and Phase Composition

The diffraction analysis confirms the successful formation of all expected phases and the structural integrity of the bifunctional catalysts. The sharp and intense CuO peaks indicate a well-crystallized structure, which is essential for catalytic activity, while the peak intensities suggest a uniform dispersion of copper oxide within the catalyst matrix. The preservation of 13X zeolite peaks confirms that the faujasite structure and its microporous properties remain intact throughout the co-precipitation and calcination processes, ensuring acid site accessibility for methanol conversion.

The formation of β -MnO₂ and K₂O crystalline domains, rather than mere surface dispersion, indicates that the permanganate precursor underwent quantitative decomposition. The presence of these phases is significant as they may influence the local electronic environment, potentially affecting the reducibility and catalytic properties of the copper phase.

Regarding the crystallite size, the CuO size obtained in this study (12.25 nm) is larger than some previously reported values (e.g., 6.30 nm). This difference may be attributed to variations in synthesis conditions, such as calcination temperature, duration, or precipitation pH. While the larger crystallite size leads to a relatively lower copper dispersion (10.45% vs 20.32%), this value remains within the optimal range for methanol synthesis applications. Furthermore, moderate dispersion might enhance catalyst stability, as highly dispersed copper particles are often more susceptible to sintering under demanding reaction conditions.

4.1.2 Surface Morphology and Composition

The SEM/EDS results provide evidence for the successful integration of methanol synthesis and acid catalysis functionalities. The confirmation of the intended 2:2:1 stoichiometry validates the reliability of the co-precipitation method used in this study.

The homogeneous mixing of copper, zinc, and aluminum at the microscopic level is particularly significant, as it is essential for creating the active sites and promoter interfaces required for optimal catalytic performance in methanol synthesis. This uniform spatial distribution suggests that the physical mixing process effectively combined the metallic oxide components with the zeolite framework, ensuring that the bifunctional nature of the catalyst is maintained throughout the structure.

4.1.3 Surface Area and Porosity (BET) Analysis

The heterogeneous nature of the catalyst morphology is typical of physically mixed bifunctional catalysts (Liu et al., 2021). The observed CZA aggregate size (10–50 μ m) is considered suitable for fixed-bed reactors as it minimizes pressure drop while maintaining mass transfer characteristics (Mahmoudi et al., 2017). The rough, cauliflower-like surface of CZA is characteristic of co-precipitated oxides and is beneficial for providing the high surface area required for methanol synthesis (Tavares et al., 2022). Furthermore, the interface between CZA and zeolite is critical for bifunctional catalysis, facilitating the conversion of intermediates (Liu et al., 2018).

The formation of rod-shaped structures in modified catalysts corresponds to β - MnO_2 phases produced during thermal decomposition (Weber et al., 2024). The preferential deposition of manganese on the zeolite surface, rather than within the matrix, aligns with findings by Kar et al. (2025). This pattern suggests that the impregnation process is governed by capillary forces and surface energy (Ramirez et al., 2019).

The significant reduction in surface area and pore volume at higher KMnO_4 loadings can be attributed to the physical occupation of the zeolite internal void space by MnO_x and K_2O species (Kar et al., 2025; Palgunadi et al., 2010). The observed textural changes suggest a pore-blocking mechanism, particularly at the pore mouth entrances, which obstructs molecular access to the internal network (Mahmoudi et al., 2017). The shift in pore size distribution at 20% loading implies that smaller pores are preferentially blocked.

These textural changes have significant implications for catalytic performance. The reduction in surface area directly correlates with a decrease in accessible acid sites within the zeolite micropores, which is expected to reduce the rates of methanol dehydration and hydrocarbon formation (Ren et al., 2019; Tavares et al., 2022). Consequently, the unmodified CZA/13X system maintains superior performance by preserving the full textural benefits of the zeolite support (Liu et al., 2018), providing a physical basis for the higher activity compared to modified counterparts (Ramirez et al., 2019).

4.1.4 Acidity Characterization

The acid site density and strength distribution of the 13X zeolite represent an optimal balance for the direct synthesis of LPG. The low-temperature sites, associated with silanol groups or weakly acidic bridging hydroxyls, provide some acidity but are generally insufficient alone for the dehydration and oligomerization required for LPG formation. In contrast, the high-temperature sites, primarily associated with bridging hydroxyl groups (Si-OH-Al) within the sodalite cages and hexagonal prisms, serve as the primary active centers for methanol dehydration.

The heterogeneity of the high-temperature peak is beneficial for LPG synthesis as it provides a range of acid strengths to catalyze different steps in the reaction network. Moderate acid strength sites are preferred for selective methanol dehydration to dimethyl ether (DME). Stronger sites facilitate C-C bond formation and chain growth.

Unlike zeolites with excessive acid strength (e.g., H-ZSM-5 or H-mordenite), which can lead to over-cracking of LPG into lighter hydrocarbons like methane and ethane, the moderate acidity of 13X minimizes these unwanted side reactions and reduces coke formation (Weber et al., 2024; Tavares et al., 2022). Furthermore, the three-dimensional pore structure combined with this balanced acidity provides shape selectivity that favors branched C_3 - C_4 hydrocarbons (Ramirez et al., 2019).

The thermal robustness indicated by the TPD profile is a decisive factor for industrial applications. Since the acid sites remain protonated at the reaction temperature of 350°C , the catalyst can maintain consistent conversion rates and selectivity during prolonged cycles (Liu et al., 2018).

4.2 Catalytic Performance Evaluation

4.2.1 CO Conversion Analysis

In contrast, the KMnO_4 -modified catalysts showed progressively decreasing CO conversions: 86.83% for CZA/10% KMnO_4 -13X and 83.14% for CZA/20% KMnO_4 -13X. From a catalytic chemistry perspective, this decrease is attributed to the disruption of the "synergistic proximity" between the methanol synthesis sites (Cu^0) and the dehydration sites (Brønsted acid sites). The introduction of MnO_2 and K_2O leads to "electronic poisoning" and "site competition". Manganese oxides, particularly β - MnO_2 , can alter the redox properties of the Cu/ZnO interface, potentially leading to the over-oxidation of active Cu^0 sites or hindering the H_2 dissociative adsorption, which is a critical step in CO hydrogenation (Palgunadi et al., 2010). Furthermore, the reduction in activity is fundamentally linked to the "methanol-intermediate inhibition." As confirmed by BET analysis, the 51% reduction in surface area for the 20% loading sample limits the diffusion of reactants to active sites. According to Le Chatelier's principle in a micro-environment, the local accumulation of methanol intermediates at the Cu surface suppresses further CO conversion rates (Ao et al., 2020). This correlates with studies on catalyst deactivation mechanisms, where pore blockage was identified as a primary cause of reduced activity.

4.2.2 Product Selectivity and Distribution

This higher selectivity of the unmodified system aligns with the mechanistic investigations by Weber et al. (2024), who emphasized that LPG formation requires a careful balance of C-C bond formation and chain growth. The acid site distribution in pristine 13X zeolite, as theoretically modeled by Tavares et al. (2022), provides the moderate acid strength necessary for selective methanol dehydration. However, the poor selectivity of the modified catalysts in this study can be rigorously explained by the "Acidity-Basicity Dualism." The decomposition of KMnO_4 releases K^+ ions that undergo ion exchange with the Brønsted acid sites (Si-OH-Al), neutralizing the sites required for the methanol-to-hydrocarbon (MTH) pathway. This reduction in "acid strength density" means the activation energy for oligomerization is no longer efficiently met, shunting the reaction towards lighter products (Weber et al. 2024). Additionally, the rod-shaped β - MnO_2 aggregates observed in SEM create a "Steric Hindrance" effect. These deposits at the zeolite pore mouths, consistent with the pore blockage model by Mahmoudi et al. (2017), create a diffusion barrier for bulky C_3 - C_4 intermediates. These molecules suffer from "restricted transition state selectivity," where increased residence time promotes secondary cracking, lowering the net LPG selectivity as documented by Ramirez et al. (2019). This further supports the findings of Liu et al. (2018), indicating that blocked acid sites lead to incomplete conversion of key intermediates.

4.2.3 Overall LPG Yield Performance

A catalytic chemistry standpoint, the drastic drop in LPG yield (nearly 50% compared to the pristine system) confirms that the "bifunctional synergy" was severely compromised by the KMnO_4 impregnation. This can be explained by the "Active Site Accessibility-Density (ASAD)" relationship. The high yield in the CZA/13X system is due to the efficient transport of methanol intermediates from the Cu-Zn-Al sites to the 13X zeolite's internal supercages. However, in the modified systems, the crystalline MnO_2 and K_2O deposits act as "diffusion bottlenecks," increasing the probability of secondary side reactions before the

intermediates can reach the critical acid sites for LPG formation (Ramirez et al., 2019). Therefore, even though syngas conversion remained relatively high, the chemical efficiency of the carbon flow toward the C₃–C₄ range was drastically reduced by the modification, highlighting that structural integrity and acid site availability are more critical than any potential alkali promotion in this specific reaction network.

4.3 Structure-Performance Relationships

The good catalytic performance of the CZA/13X system arises from the synergistic combination of several key structural factors that create suitable conditions for bifunctional catalysis, as demonstrated by comprehensive studies conducted by Liu et al. (2018). The optimal acid-metal balance represents perhaps the most critical aspect of this system's success, which aligns with theoretical frameworks developed by Weber et al. (2024). The moderate acid strength of 13X zeolite provides sufficient driving force for methanol dehydration and subsequent oligomerization reactions while avoiding excessive cracking. From a catalytic chemistry perspective, this "Acidity Tuning" is the heart of LPG selectivity; by utilizing the moderate Brønsted acidity of 13X, the reaction pathway is successfully steered toward C₃–C₄ hydrocarbons rather than lighter alkanes (CH₄, C₂H₆) which often dominate over stronger acid catalysts like H-ZSM-5 (Tavares et al., 2022).

The three-dimensional pore network of 13X zeolite contributes significantly to the observed selectivity through both geometric and diffusion effects. The supercage dimensions provide adequate space for the formation and diffusion of LPG molecules while imposing shape selectivity constraints that favor branched C₃–C₄ products over linear longer-chain hydrocarbons (Mahmoudi et al., 2017). This "Transition State Selectivity" is maintained only when the pore mouths are unobstructed, allowing for the rapid egress of bulky branched isomers before they undergo secondary cracking (Ramirez et al., 2019). The unhindered accessibility of active sites in the unmodified system ensures minimal diffusion path lengths for intermediate species (methanol/DME) while maintaining the distinct chemical environments required for each catalytic function (Kar et al., 2025).

The most critical issue is the progressive pore blockage induced by the deposition of MnO₂ and K₂O species. This 'physical shielding' creates a significant bottleneck within the reaction network, leading to the formation of a 'methanol-rich micro-environment' at the Copper (Cu) surface. Such localized concentrations thermodynamically inhibit further CO conversion, effectively stalling the reaction sequence. Furthermore, the introduction of Potassium (K) species serves as an 'alkali poison' to the zeolite's Brønsted acid sites. Through an ion-exchange process, where H⁺ ions are replaced by K⁺, the acid site density is substantially depleted. Consequently, the 'chemical pressure' necessary to drive the Methanol-to-Hydrocarbon (MTH) pathway is insufficient, as supported by the findings of Ao et al. (2020). Finally, the spatial distribution of these deposits, as observed via SEM, reveals a highly heterogeneous surface. This confirms that the deleterious effects of the modification are cumulative rather than compensatory, reinforcing the conclusions drawn by Liu et al. (2018) regarding the impact of non-uniform surface properties on catalytic efficiency.

The structure-performance relationships revealed in this study demonstrate that maintaining a "Clean Interface" between the metallic CZA and the acidic 13X is far more critical than individual

component modification. This systems-level insight suggests that for high-performance syngas-to-LPG catalysts, the design strategy must prioritize the preservation of native microporosity and acid strength over the introduction of complex transition metal promoters that may introduce unwanted steric and electronic complications (Ramirez et al., 2019).

5. Conclusion

This investigation of bifunctional catalysts for direct LPG synthesis from syngas has provided valuable insights into the importance of maintaining optimal structural properties for effective catalytic performance. The systematic comparison of unmodified and KMnO_4 -modified CZA/13X systems has revealed fundamental principles that govern the success of bifunctional catalysis. The unmodified CZA/13X catalyst demonstrated superior performance across all measured metrics, achieving 87.64% CO conversion, 38.16% LPG selectivity, and 33.47% LPG yield under the optimized conditions (350°C, 40 bar). These results represent a significant advantage over the KMnO_4 -modified alternatives, suggesting that the pristine bifunctional interface is more effective for industrial LPG production.

The structural characterization provided clear evidence for the mechanisms underlying these differences. While XRD confirmed the formation of all expected phases, it revealed that KMnO_4 decomposition produces crystalline MnO_2 and K_2O . From a catalytic chemistry perspective, these species did not act as effective promoters but rather as “catalytic poisons” that disrupted the active site architecture. SEM and BET analyses quantified a dramatic loss of surface area (up to 51%) and pore volume (47%) for the 20% KMnO_4 -loaded system. This physical degradation creates a “diffusion bottleneck” that hinders the transport of methanol intermediates from Cu sites to the zeolite acid sites, thereby breaking the “bifunctional synergy” required for continuous CO hydrogenation.

The catalytic evaluation revealed that KMnO_4 modification negatively impacts both CO conversion and LPG selectivity. The chemical evidence suggests that K^+ ions from the promoter underwent ion exchange with Brønsted acid sites (Si-OH-Al), neutralizing the sites essential for the methanol-to-hydrocarbon (MTH) pathway. This “alkali poisoning” effect, combined with the steric hindrance from rod-shaped β - MnO_2 deposits at pore mouths, shunted the reaction pathway toward lighter gaseous products and limited the formation of bulky C_3 - C_4 hydrocarbons.

The structure-performance relationships identified in this study demonstrate that the performance of the unmodified CZA/13X system results from the synergistic combination of optimal acid-metal balance, favorable pore structure characteristics, unhindered active site accessibility, and thermal stability. The moderate acid strength of 13X zeolite provides sufficient activity for methanol dehydration without causing excessive cracking. The fundamental chemical insight gained is that maintaining a “clean and accessible interface” between the metallic and acidic functions is more critical than chemical modification that introduces unwanted steric and electronic complications.

Future research should focus on exploring promoters that can enhance metal dispersion without occupying the critical internal pore volume or neutralizing the active acid sites of the zeolite. Additionally,

investigating long-term stability and resistance to poisoning under industrial conditions will further enhance the commercial viability of this technology. These fundamental insights provide a solid foundation for the continued development of bifunctional catalysis in sustainable fuel production.

6. Acknowledgment

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