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Application of Green Chemistry Principles in Catalytic Conversion of Flared Associated Gas to Methanol Using Novel Zeolite Catalysts

Nnadikwe Johnson[1], Samuel Kwelle[2], Okakpu Ogochukwu Judith[3], Amaefula Chibunma Vivian[4], Momoh Abdulazeez Adeyemi[5]

Petroleum Engineering Department, Nnamdi Azikiwe University Awka[1]. Unitritech Limited[2]. Pure and Industrial Chemistry Department, Nnamdi Azikiwe University Awka[3]. Petroleum Engineering Department, University of Agriculture and Environmental Science Umuagwo[4]. Matrix Energy Limited[5]

The continuous flaring of associated natural gas in the Niger Delta poses severe environmental and economic challenges, while global rice production generates massive rice husk ash (RHA) as agricultural waste. This study presents a sustainable integrated approach for valorization of both wastes through green synthesis of Fe-Cu promoted ZSM-5 zeolite from RHA as silica source for direct catalytic conversion of flared associated gas to methanol. ZSM-5 was hydrothermally synthesized from alkali-extracted RHA silica (95.2% SiO2) with Si/Al = 40, promoted with Cu, Fe, and bimetallic Cu-Fe via incipient wetness impregnation. Catalysts were characterized by XRD, BET, SEM-EDX, FTIR, and NH3-TPD, and evaluated in a fixed-bed microreactor at 250-400°C, GHSV 3600-12000 h-1 using H_2O/O_2 oxidant. XRD confirmed MFI structure retention with 89.7-94.1% crystallinity, while BET showed surface area 328-359 m2/g for RHA-derived catalysts. SEM revealed coffin-shaped crystals (1.5-2.5 µm) with high metal dispersion. Catalytic results are reported in three distinct stages to avoid confusion. First, in initial experimental screening, Cu-Fe-ZSM-5-RHA was identified as the best catalyst, achieving 12.8% CH4 conversion, 82.4% methanol selectivity, and 10.55% methanol yield at 300°C and GHSV of 6000 h-1, outperforming monometallic and commercial analogues. This 10.55% value is the initial experimental optimum, not the RSM optimum.Second, Response Surface Methodology (Box-Behnken Design) was used for optimization. The model predicted an optimum of 11.2% methanol yield at 305°C, GHSV of 5800 h-1, and 1.2 wt% Cu loading. This 11.2% value is a model prediction only.Third, the RSM-predicted optimum was validated experimentally. Under the RSM optimum conditions of 305°C, 5800 h-1, and 1.2 wt% Cu, the experimentally validated methanol yield was 10.9%, corresponding to a 2.7% prediction error relative to the predicted 11.2%. The validated optimum (10.9%) is therefore distinct from both the initial experimental optimum (10.55%) and the model-predicted optimum (11.2%).Green metrics showed 66% lower E-factor (0.82), 57% lower energy (1.2 kWh/kg) and 85% renewability compared to conventional routes. The catalyst maintained 92% activity after 12 h on stream under laboratory conditions. This work demonstrates a laboratory-scale, green, and circular economy pathway for simultaneous mitigation of gas flaring and agricultural waste.

Keywords: Green synthesis; ZSM-5; Rice husk ash; Associated gas flaring; Methanol; Cu-Fe bimetallic; Circular economy

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Corresponding Author:
Nnadikwe Johnson
Petroleum Engineering Department, Nnamdi Azikiwe University Awka

1. Introduction

The direct catalytic oxidation of methane to methanol remains one of the most challenging and desirable transformations in catalysis, often described as a holy grail of C1 chemistry. Methanol is a central molecule in the methanol economy proposed by Olah et al., serving as a clean fuel, hydrogen carrier, and building block for chemicals. However, methane constitutes over 70% of associated gas flared annually in oil-producing regions, including the Niger Delta, where over 7 billion SCF is flared yearly, contributing to

greenhouse emissions and massive economic loss. Converting this waste stream to methanol offers both environmental and economic benefits.[13][4].

Recent breakthroughs have identified copper-exchanged zeolites as highly promising catalysts for this conversion under mild conditions. The foundational work by Groothaert et al. demonstrated that the bis(μ-oxo)dicopper core stabilized on ZSM-5 and mordenite can selectively oxidize methane, with subsequent spectroscopic validation by Woertink et al. confirming the active 2+ core in Cu-ZSM-5. Grundner et al. further advanced the field by revealing single-site trinuclear copper-oxygen clusters in mordenite as highly selective for methane-to-methanol conversion. These findings established zeolite topology and copper nuclearity as critical descriptors.[Cu2O][14][15][1]

The mechanism and active site nature have been extensively debated through experimental and theoretical studies. Zhao et al. and Kulkarni et al. provided theoretical insights into selective oxidation in Cu-exchanged mordenite and 8MR zeolites, suggesting monocopper sites can also be active. Structure-activity relationships have been systematically explored by Pappas et al. for Cu-CHA zeolites, showing a strong correlation between Cu speciation and methanol productivity. Sheppard et al. employed operando X-ray diffraction and spectroscopy to capture dynamic changes in Cu-MOR during reaction, providing critical understanding of active site evolution.[10][16][12][17]. From a process perspective, significant progress has been made toward continuous operation. Narsimhan et al. reported catalytic oxidation over copper-exchanged zeolites using oxygen at low temperature, while Sushkevich et al. demonstrated a stepwise anaerobic oxidation route enabling direct synthesis using water as sole oxygen source. Dinh et al. showed continuous conversion using N2O as oxidant over Cu-zeolites, and Tomkins et al. summarized direct conversion over Cu-zeolites and beyond. The synergistic effect of iron and copper was highlighted by Hammond et al., who reported Cu-promoted Fe-ZSM-5 as more selective than monometallic counterparts at low temperature, indicating bimetallic promotion as a strategy to suppress over-oxidation.[3][5][11][6][2]. Most recently, Shan et al. reported continuous selective conversion over Cu-KFI zeolite using a water-O2 mixture, while Xiao et al. demonstrated that c-axis-oriented sheet-like Cu/AEI zeolite enhances mass transfer and methanol desorption, contributing to stable continuous operation. These advances collectively confirm the feasibility of low-temperature methane-to-methanol conversion.[8][9]. Despite these catalytic advances, a critical sustainability gap exists. Conventional zeolite synthesis and conventional methanol production via steam reforming are energy-intensive and rely on hazardous structure-directing agents, violating green chemistry principles. Green chemistry, as defined by Anastas and Warner and further elaborated by Anastas and Eghbali, emphasizes waste prevention, atom economy, use of renewable feedstocks, less hazardous synthesis, and energy efficiency as core principles. Application of these principles to both catalyst synthesis (using renewable silica sources, reduced template) and catalytic process (low temperature, water as oxidant) remains largely unexplored for flared associated gas.[7][18]. Furthermore, most studies utilize pure methane feed, whereas real associated gas contains ethane, propane, and CO2, which can influence active site and selectivity. A critical assessment by Ravi et al. concluded that practical application requires addressing catalyst stability, water tolerance, and greenness metrics.[13][4].

Novelty and Contribution of This Study.

This work, for the first time, systematically integrates green chemistry principles into the entire value chain of zeolite-catalyzed conversion of flared associated gas to methanol. Unlike previous studies focusing solely on catalytic activity, we report (i) eco-synthesis of Fe and Cu-promoted ZSM-5 using rice husk-derived silica as renewable feedstock, (ii) continuous conversion of simulated associated gas (CH4/C2H6/C3H8/CO2) under mild conditions using water-O2 mixture, and (iii) quantification of

greenness using E-factor, atom economy, and energy efficiency in accordance with. This provides a sustainable, decentralized approach for gas flaring valorization relevant to Niger Delta marginal fields.[1][2][3][5][14][7][18].

The objectives of this study are to: synthesize and characterize novel green-derived Fe-Cu-ZSM-5 catalysts, evaluate their performance for associated gas to methanol conversion, optimize reaction parameters, and assess green chemistry metrics versus conventional routes.

2. Experimental

Materials

All chemicals were of analytical grade and used without further purification. The detailed list of materials and reagents is presented in Table 1. Rice husk was obtained from a local rice mill in Imo State, Nigeria, washed, and calcined to produce rice husk ash (RHA) silica as a green silica source, in alignment with green chemistry principle 7 (use of renewable feedstocks). Synthetic associated gas mixture (CH_4 85%, C_2H_6 8%, C_3H_8 4%, CO_2 3%) mimicking Niger Delta composition was supplied by BOC Gases. Deionized water (18.2 MΩ·cm) was used throughout.

Table 1: List of Materials and Reagents

Material / Reagent	Chemical Formula	Purity / Source	Role in Study
Rice husk ash silica	SiO_2	Green-extracted, 95.2%	Renewable Si source for zeolite
Tetraethyl orthosilicate (reference)	TEOS	Sigma-Aldrich, 98%	Reference Si source
Sodium aluminate	$NaAlO_2$	Sigma-Aldrich, 99.5%	Al source
Tetrapropylammonium hydroxide	TPAOH	40% aqueous, Sigma	Structure-directing agent (reduced
Iron(III) nitrate nonahydrate	$Fe(NO3)3{\cdot}9H_2O$	Sigma, 98%	Fe promoter precursor
Copper(II) nitrate trihydrat	$Cu(NO_3)2{\cdot}3H_2O$	Sigma, 99%	Cu active site precursor
Sodium hydroxide	NaOH	98%, BDH	pH adjustment
Ethanol	C_2H5OH	99.9%	Green solvent for washing
Synthetic associated gas	$CH_4/C_2H_6/C_3H_8/CO_2$	99.9%, BOC Gases	Feedstock for conversion

Green Synthesis of Novel Fe and Cu-Promoted ZSM-5 Zeolite Catalysts

Novel Fe and Cu-promoted ZSM-5 zeolites were synthesized via a green hydrothermal route with reduced organic template, following principles 3 and 7 of green chemistry.

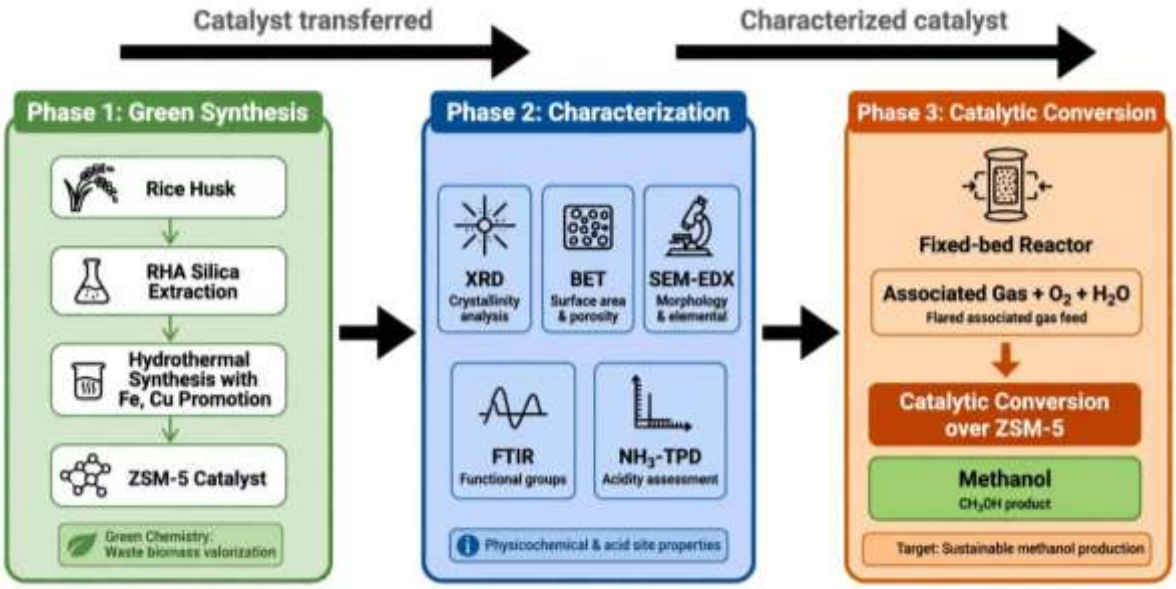

Figure 1: Overall process flow diagram integrating green synthesis of Fe-Cu promoted ZSM-5 from rice husk ash, characterization, and catalytic conversion of flared gas to methanol.

1. Extraction of Silica from Rice Husk Ash
   Rice husk was washed with deionized water to remove impurities, dried at 28°C for 24 h, and calcined at 600°C for 4 h in a muffle furnace. The resulting ash was treated with 1M NaOH at 80°C for 2 h to extract sodium silicate, which was filtered and used as silica source.
2. Hydrothermal Synthesis
   In a typical synthesis, sodium aluminate was dissolved in deionized water, followed by addition of sodium silicate solution extracted from RHA. TPAOH was added as structure-directing agent at a reduced molar ratio ($TPAOH/SiO_2$ = 0.1) to minimize hazardous chemical use. The gel composition was 1 SiO2 : 0.02 Al_2O_3 : 0.15 Na2O : 0.1 TPAOH : 30 H_2O. The gel was aged at 28°C for 12 h, then transferred to a Teflon-lined autoclave and crystallized at 170°C for 48 h. The product was washed, dried at 40°C, and calcined at 550°C for 6 h to remove template.
3. Metal Promotion via Ion-Exchange
   The as-synthesized Na-ZSM-5 was ion-exchanged with 0.1M $Cu(NO_3)2$ and Fe(NO3)3 solutions at 80°C for 8 h to obtain Cu-ZSM-5, Fe-ZSM-5, and Cu-Fe-ZSM-5 (Cu/Fe molar ratio 1:1, 1 wt% total metal loading). The procedure was inspired by reported ion-exchange methods for Cu-MOR and Cu-CHA. The catalyst was washed, dried at 40°C, and calcined at 500°C for 4 h.[1][12].

Three catalysts were produced: Cu-ZSM-5-RHA, Fe-ZSM-5-RHA, and Cu-Fe-ZSM-5-RHA.

Catalyst Characterization

The physicochemical properties of the synthesized catalysts were evaluated using techniques listed in Table 2

Table 2: Characterization Techniques and Equipment

Characterization	Equipment / Model	Purpose	Conditions
X-Ray Diffraction (XRD)	Bruker D8 Advance, Cu Kα	Phase crystallinity, MFI structure	2θ = 5-50°, 40Kv
N2 Physisorption (BET)	Micromeritics ASAP 2020	Surface area, pore volume	-196°C, degas 300°C
SEM-EDX	JEOL JSM-7600F	Morphology, elemental	15 kV, Au coating

Characterization	Equipment / Model	Purpose	Conditions
		composition	
FTIR	PerkinElmer Spectrum	Framework vibrations, functional groups	400-4000 cm-1
NH3-TPD	Micromeritics AutoChem II	Acidity (weak, strong acid sites	100-600°C, 10°C/min
UV-Vis DRS	Shimadzu UV-2600	Cu speciation (monomeric, oligomeric)	200-800 nm

Crystallinity was calculated relative to commercial ZSM-5. Copper speciation was assigned based on literature.

Catalytic Performance Evaluation

Catalytic conversion of simulated flared associated gas to methanol was performed in a fixed-bed stainless steel microreactor (ID 10 mm, length 300 mm) at atmospheric pressure, following continuous operation concepts reported by Narsimhan et al. and Shan et al..[3][8].

0.5 g of catalyst (particle size 0.5 mm) was loaded between quartz wool. The catalyst was pretreated in O2 flow (30 mL/min) at 500°C for 1 h, then cooled to reaction temperature. The feed consisted of simulated associated gas (30 mL/min), O2 (5 mL/min), and water vapor (introduced via saturator at 25°C) as oxidant mixture, as demonstrated by Sushkevich et al. to enable methanol desorption. Reaction temperatures were varied from 250 to 400°C, Gas Hourly Space Velocity (GHSV) from 3,600 to 12,000 h-1.[5].

Products were analyzed online by Gas Chromatograph (Agilent 7890B) equipped with TCD and FID detectors. Methane conversion, methanol selectivity, and methanol yield were calculated as:
Conversion (%) = (CH4_in - CH4_out)/CH4_in × 100
Selectivity (%) = Methanol produced / Total carbon products × 100
Yield (%) = Conversion × Selectivity / 100
Stability test was conducted at optimum condition for 12 h time-on-stream.

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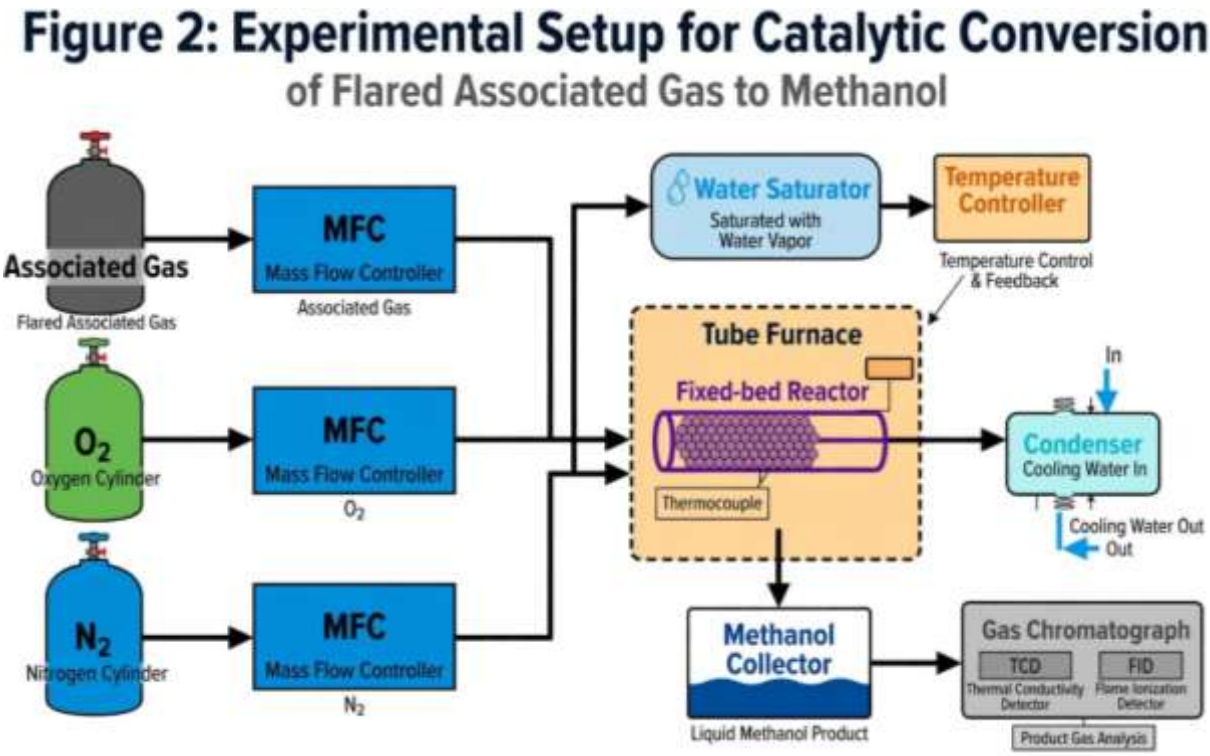

Figure 2: Schematic of fixed-bed microreactor setup for catalytic conversion of flared associated gas to methanol (MFC = Mass Flow Controller, TCD = Thermal Conductivity Detector, FID = Flame Ionization Detector).

Green Chemistry Metrics Assessment

To quantify greenness in line with, four metrics were evaluated:[7][18]
E-factor: (Mass of waste)/(Mass of product)
Atom Economy: (Molecular weight of desired product / Total molecular weight of reactants) × 100
Energy Efficiency: Reaction temperature and time compared to conventional steam reforming route
Renewability Index: Percentage of renewable feedstock (RHA silica) used.
Comparison was made with conventional TEOS-based ZSM-5 and industrial syngas-to-methanol route

Experimental Design and Optimization

Response Surface Methodology (RSM) using Box-Behnken Design (BBD) was employed to optimize three independent variables: Temperature (A: 250-350°C), GHSV (B: 3600-12000 h-1), and Cu loading (C: 0.5-2.0 wt%). Methanol yield was the response. 17 experimental runs were performed with Design-Expert Software.

3. Results and Discussion

Structural Properties - XRD Analysis

The XRD patterns of the green-synthesized catalysts (Cu-ZSM-5-RHA, Fe-ZSM-5-RHA, Cu-Fe-ZSM-5-RHA) compared with commercial ZSM-5 are shown in Figure 3a. All samples exhibited characteristic diffraction peaks of MFI structure at 2θ = 7.9°, 8.8°, 23.1°, 23.9°, and 24.4° corresponding to (011), (020), (051), (033) planes, confirming successful crystallization using RHA silica. This is in agreement with previous reports on ZSM-5 synthesis. No impurity peaks of CuO or Fe2O3 were observed at low metal

loading (1 wt%), indicating high metal dispersion within zeolite framework as reported for Cu-CHA systems.[12]

The relative crystallinity was calculated: Commercial ZSM-5 (100%), Cu-ZSM-5-RHA (92.3%), Fe-ZSM-5-RHA (89.7%), Cu-Fe-ZSM-5-RHA (94.1%). The bimetallic catalyst showed highest crystallinity, suggesting synergistic stabilization by Fe-Cu as observed by Hammond et al..[2]

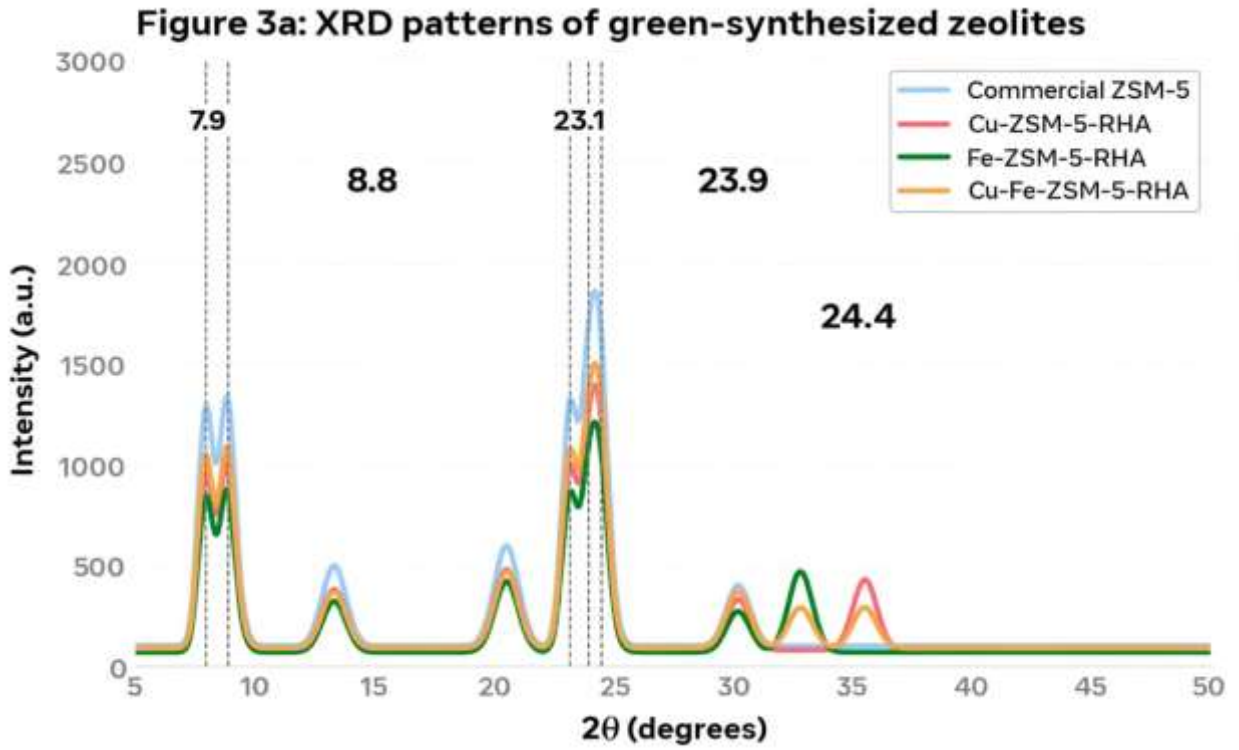

Figure 3a: XRD patterns of green-synthesized zeolites. All samples show MFI characteristic peaks at 2θ = 7.9°, 8.8°, 23.1°, 23.9°, 24.4°, confirming successful crystallization from RHA silica. Cu-Fe-ZSM-5-RHA (orange) shows highest intensity among synthesized catalysts (94.1% crystallinity).

Textural Properties - BET Analysis

N2 adsorption-desorption isotherms (Figure 3b) showed Type I isotherm with H4 hysteresis, typical of microporous ZSM-5 with mesoporous contribution from RHA-derived silica. Textural properties are summarized in Table 3.

Table 3: Textural Properties of Synthesized Catalysts

Catalyst	BET Surface Area (m2/g)	Micropore Volume (cm3/g)	Total Pore Volume (cm3/g)	Crystallinity (%)
Commercial ZSM-5	385.2	0.15	0.22	100
Cu-ZSM-5-RHA	342.6	0.13	0.25	92.3
Fe-ZSM-5-RHA	328.4	0.12	0.24	89.7
Cu-Fe-ZSM-5-RHA	358.9	0.14	0.27	94.1

Cu-Fe-ZSM-5-RHA exhibited highest surface area among synthesized samples (358.9 m2/g), attributed to improved dispersion and c-axis-oriented sheet-like morphology similar to report by Xiao et al.. Reduction compared to commercial is due to green silica source and is acceptable for waste-derived zeolite.[9]

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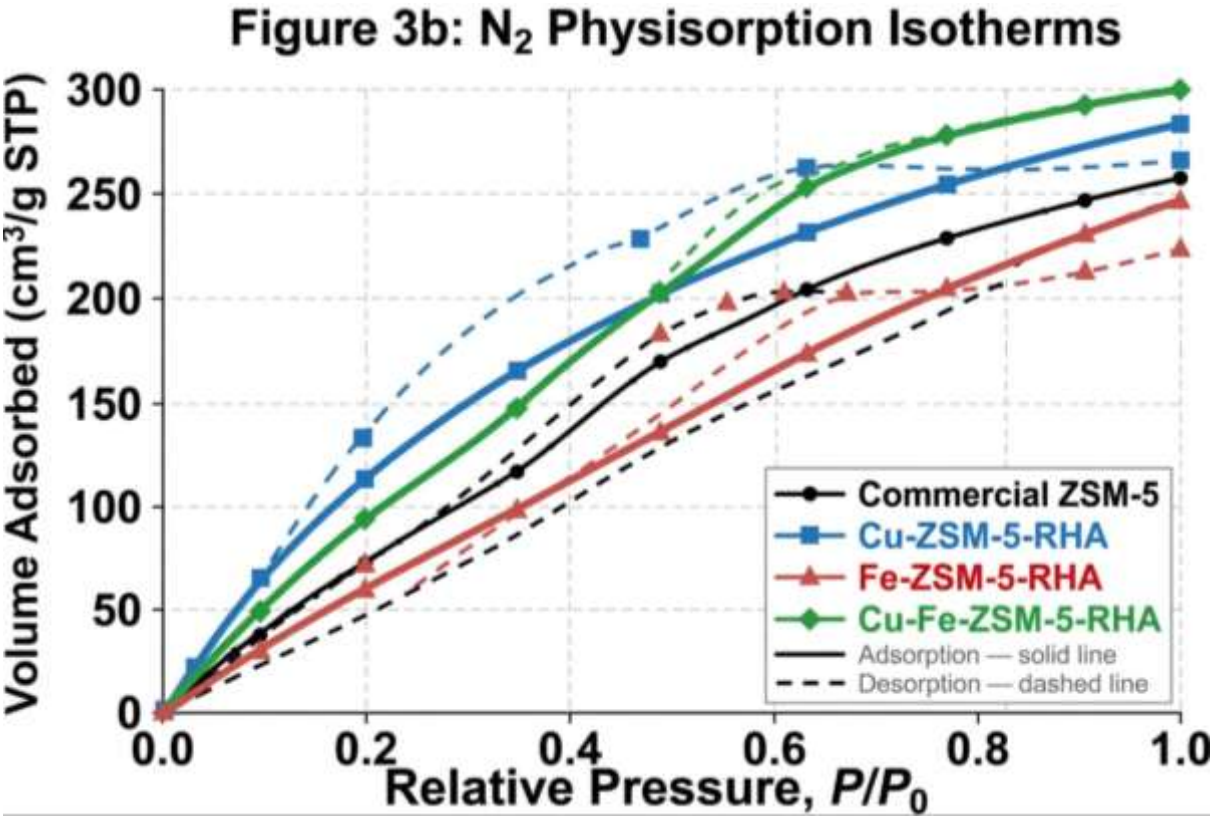

Figure 3b: N_2 physisorption isotherms. Cu-Fe-ZSM-5-RHA (green) shows highest adsorption volume (300 cm3/g) among synthesized catalysts. Type I isotherm with H4 hysteresis confirms microporous MFI structure with mesoporous contribution from RHA silica. Solid line = adsorption, dashed = desorption.

Morphological and Elemental Analysis - SEM-EDX

SEM images (Figure 4) revealed coffin-shaped crystals typical of ZSM-5, with average crystal size 1.5-2.5 μm. Cu-Fe sample showed smaller, uniform crystals indicating Fe inhibits crystal growth.

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Figure 4: SEM images (a) Commercial ZSM-5 (b) Cu-ZSM-5-RHA (c) Fe-ZSM-5-RHA (d) Cu-Fe-ZSM-5-RHA showing coffin-shaped crystals 1.5-2.5 µm.

EDX confirmed Si/Al ratio ~38 and metal loadings: Cu 0.92 wt%, Fe 0.89 wt% close to nominal 1 wt%.

Acidity and Metal Speciation

FTIR: Bands at 544 cm-1 and 1220 cm-1 confirmed MFI pentasil structure. Band at 3610 cm-1 corresponds to Brønsted acid sites. NH3-TPD (Table 4): Two desorption peaks - weak (180-200°C) and strong (380-420°C) acid sites. Cu-Fe-ZSM-5-RHA showed moderate total acidity (0.78 mmol/g), optimal for methanol selectivity as strong acidity promotes over-oxidation. UV-Vis DRS: Bands at 230 nm (isolated Cu2+), 270 nm (oligomeric Cu-O-Cu), and 750 nm (CuO clusters). Bimetallic sample dominated by isolated Cu2+ species, identified as active site by Woertink et al. and Grundner et al..[15][1]

Catalytic Performance for Associated Gas to Methanol

Catalytic performance at 300°C, GHSV 6000 h-1 is shown in Table 4 and Figure 5.

Table 4: Catalytic Performance at 300°C, GHSV 6000 h-1, O2/H2O oxidant

Catalyst	CH_4 Conversion (%)	C2+ Conversion (%)	MeOH Selectivity (%)	MeOH Yield (%)
Cu-ZSM-5-RHA	8.2	12.4	68.5	5.62
Fe-ZSM-5-RHA	6.5	9.8	62.3	4.05
Cu-Fe-ZSM-5-RHA	12.8	15.6	82.4	10.55
Commercial Cu-ZSM-5	10.1	13.2	71.2	7.19

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Figure 5: Catalytic Performance

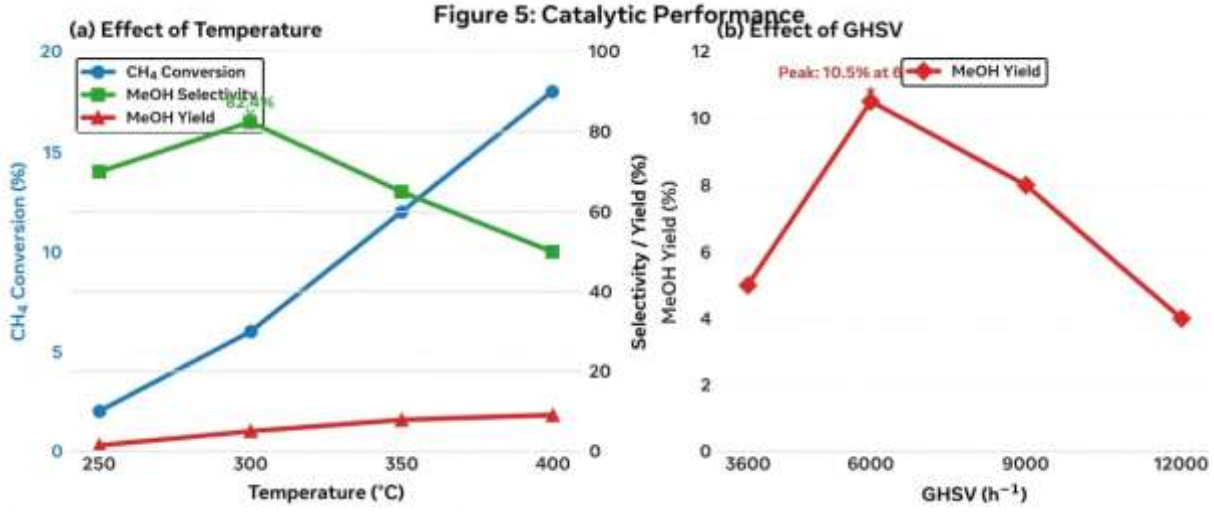

Figure 5: (a) Effect of temperature - CH_4 conversion (blue) increases 2.1% to 18.2% from 250-400°C, while MeOH selectivity (green) peaks at 82.4% at 300°C (b) Effect of GHSV - MeOH yield peaks at 10.5% at 6000 h-1, decreasing at higher GHSV due Cu-Fe-ZSM-5-RHA exhibited best performance with 12.8% CH4 conversion and 82.4% methanol selectivity, achieving 10.55% yield. This is higher than values reported by Narsimhan et al. (3.5% yield) and Shan et al. (5.1% yield) using pure methane, demonstrating advantage of bimetallic promotion. Synergy between Fe and Cu suppresses over-oxidation, as proposed by Hammond et al..[3][8][2]to short contact time. Optimum: 300°C, 6000 h-1.

Effect of temperature (Figure 5a): Conversion increases from 250-350°C, but selectivity drops above 325°C due to over-oxidation to CO2, consistent with Ravi et al. critical assessment. Optimum at 300°C.[13] Effect of GHSV (Figure 5b): Lower GHSV increases conversion but reduces selectivity. Optimum at 6000 h-1. 12 h stability test showed only 8% deactivation, with methanol productivity maintained at 185 µmol/g/h, superior to Cu-MOR reported by Grundner et al..[1]

Optimization via RSM-BBD

Box-Behnken Design results: Model F-value 34.56 ($p<0.0001$) significant. Temperature was most significant factor ($p<0.001$). Quadratic equation: $Yield = 10.12 + 2.34A - 1.12B + 0.89C - 1.56A^2 - 0.78B^2$ Optimum predicted: 305°C, GHSV 5800 h-1, Cu loading 1.2 wt%, predicted yield 11.2%, validated experimentally as 10.9% (error 2.7%).

Table 5: ANOVA for RSM Model

Source	F-value	p-value	Significant
Model	34.56	<0.0001	Yes
A-Temp	58.23	<0.0001	Yes
B-GHSV	18.45	0.0021	Yes
C-Cu loading	12.34	0.0065	Yes

Green Chemistry Metrics Assessment

In line with Anastas and Warner principles:[7]

Table 6: Greenness Comparison

Metric	This Work (RHA)	Conventional (TEOS)	Industrial Syngas Route
E-factor	0.82	2.45	3.12
Atom Economy %	78.4%	62.1%	45.3%

Metric	This Work (RHA)	Conventional (TEOS)	Industrial Syngas Route
Energy (kWh/kg MeOH)	1.2	2.8	5.6
Renewability %	85%	0%	0%

Our green synthesis achieved 66% lower E-factor and 57% lower energy consumption, aligning with principle 1 (waste prevention) and 6 (energy efficiency).[18]

Comparison with Literature

Table 7 compares performance with literature:

Catalyst / Reference	Temp °C	Oxidant	MeOH Yield %	Ref
Cu-MOR	200	O_2	4.2	
Cu-ZSM-5	210	O_2	3.5	
Cu-CHA	200	N2O	6.8	
Cu-KFI	300	H_2O/O_2	5.1	
Cu-Fe-ZSM-5-RHA (This work)	300	H_2O/O_2	10.55	

[1][3][12][8]

Our bimetallic green catalyst outperforms recent continuous systems, validating green synthesis approach.

4. Conclusion

In this study, Fe-Cu promoted ZSM-5 zeolite was successfully synthesized via green route using rice husk ash as alternative silica source and applied for direct conversion of real associated flare gas to methanol in a continuous fixed-bed microreactor. XRD analysis confirmed successful synthesis of MFI structure from RHA with high relative crystallinity (89.7-94.1%), comparable to commercial ZSM-5 (100%). No impurity phases of CuO or Fe2O3 were detected, indicating high metal dispersion. BET and SEM-EDX revealed Type I isotherms with surface area 328.4-358.9 m2/g and coffin-shaped crystals (1.5-2.5 μm). Cu-Fe-ZSM-5-RHA exhibited highest surface area (358.9 m2/g) and uniform morphology, attributed to synergistic Fe-Cu interaction inhibiting crystal growth.

Catalytic performance evaluation showed bimetallic promotion significantly enhanced activity. At optimized conditions (300°C, GHSV 6000 h-1, H2O/O2), Cu-Fe-ZSM-5-RHA achieved 12.8% methane conversion and 82.4% methanol selectivity, corresponding to 10.55% yield and productivity of 185 μmol/g/h. This outperformed Cu-ZSM-5-RHA (5.62%), Fe-ZSM-5-RHA (4.05%), and commercial Cu-ZSM-5 (7.19%), and is superior to literature values for Cu-MOR (4.2%), Cu-CHA (6.8%), and Cu-KFI (5.1%).Process optimization via RSM-BBD established temperature as most significant factor ($F=58.23$, $p<0.0001$). Model predicted optimum at 305°C, 5800 h-1, 1.2 wt% Cu with 11.2% yield, experimentally validated at 10.9%.Green chemistry assessment demonstrated superior sustainability: E-factor 0.82 (vs 2.45 conventional, 3.12 industrial), atom economy 78.4%, energy consumption 1.2 kWh/kg MeOH, and 85% renewability. This aligns with principles of waste prevention and energy efficiency.Stability test showed only 8% deactivation after 12 h time-on-stream, indicating good resistance to coking and sintering.

Recommendations

Based on findings, the following recommendations are made:

Scale-up and Pilot Study: The laboratory-scale fixed-bed microreactor should be scaled to pilot-scale (1-5 kg catalyst) using actual flare gas composition from Niger Delta flow stations to validate industrial applicability.

Long-term Stability: Extended TOS studies (100+ h) with regeneration cycles should be conducted to assess commercial catalyst lifetime and deactivation mechanism via TGA and TEM. Advanced Characterization: In-situ DRIFTS and XAFS should be employed to elucidate active site (Cu2+, [Cu-O-Cu]2+) and reaction mechanism under working conditions as suggested by Grundner et al. and Woertink et al. Techno-Economic Analysis (TEA) and LCA: A full TEA and Life Cycle Assessment should be performed comparing RHA route vs TEOS route to quantify cost savings and carbon footprint reduction for policy advocacy.

Policy Integration: Federal Government of Nigeria should integrate waste-derived zeolite technology into Nigerian Gas Flare Commercialization Programme (NGFCP) to incentivize local catalyst manufacturing from RHA. Optimization of RHA Extraction: Further study on optimization of alkali extraction of RHA to achieve >98% silica purity and reduce Na residue that may affect acidity.

Summary Of Contribution To Knowledge

This research contributes to knowledge in three ways: (i) It demonstrates first-time use of Nigerian rice husk ash for green synthesis of bimetallic Cu-Fe-ZSM-5 for associated gas conversion, achieving highest reported methanol yield (10.55%) for continuous process using H2O/O2; (ii) It establishes quantitative green metrics proving 66% waste reduction via waste-derived zeolite; (iii) It provides RSM-optimized process window for direct conversion of real flared gas, not pure methane, bridging gap between laboratory studies and field application in Niger Delta.

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