ECO-SUSTAINABILITY OF Zn–Cu–O CATALYSTS FOR ETHANOL DEHYDROGENATION

Selime Mammadova[a*], Vilayet Mammadov[b], Ali Ali-zade[a], Elmir Babayev[b,c], Sevinj Namatova

[a]Azerbaijan State Oil and Industry University, Azadlıq 20, Baku AZ-1010, Azerbaijan,
[b]Institute of Catalysis and Inorganic Chemistry, H. Javid Str.29.AZ1143 Baku, Azerbaijan
[c]Baku Engineering University, H.Aliyev 120, AZ0101, Khirdalan Azerbaijan
salimaabbaszade@mail.ru

Abstract

This work investigates the eco-reliability of zinc–copper oxide (Zn–Cu–O) binary catalysts in ethanol dehydrogenation, emphasizing the link between structural characteristics, catalytic activity, and environmental performance. Ethanol dehydrogenation yields valuable products such as acetaldehyde, ethyl acetate, and ethylene, which represent cleaner alternatives to petrochemical-based syntheses. Experimental results demonstrate that the Zn/Cu atomic ratio strongly affects catalytic behavior: zinc-rich catalysts enhance both activity and selectivity toward acetaldehyde, ensuring process stability. X-ray diffraction confirmed ZnO and CuO phases as dominant structures, while increasing zinc content improved crystallinity, which correlates with higher product selectivity and more predictable performance. The catalysts' specific surface area, measured by nitrogen thermal desorption (3.5–8.0 m²/g), influenced yields differently, indicating that surface parameters play a critical role in ecological efficiency by reducing energy consumption and undesired by-products. These findings highlight Zn–Cu–O binary catalysts as reliable and environmentally sound systems, where structural parameters—crystallinity, Zn/Cu ratio, and surface area—serve as predictors of both catalytic reliability and ecological sustainability in low-carbon ethanol upgrading. Keywords: Reliability; Eco-sustainability; Structure–activity relationships; Zn–Cu–O catalysts; Ethanol dehydrogenation; Green chemistry.

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I. Introduction

Bioethanol is widely recognized as a promising renewable feedstock for the production of high-value chemical intermediates and cleaner fuels within the framework of green chemistry [1–2]. Beyond its role as a sustainable energy carrier, bioethanol utilization is essential for mitigating greenhouse gas emissions and reducing dependence on fossil-based resources. Considerable attention has been devoted to catalytic pathways and design approaches for ethanol upgrading toward higher-value C_4+ products, where acid–base cooperation, metal–support electronic effects, and controlled regulation of reaction intermediates play decisive roles [3–4, 13]. Through ethanol dehydrogenation, a variety of valuable products can be obtained, including diethyl ether ($(C_2H_5)_2O$), acetic acid (CH_3COOH), ethyl acetate ($CH_3COOC_2H_5$), acetaldehyde (CH_3CHO), and acetone (CH_3COCH_3), among others [5–8, 21].

A broad spectrum of catalytic systems has been developed for ethanol dehydrogenation, ranging from noble metals (Pt, Pd, Rh, Ru, Ag) supported on oxides [11, 14, 16, 18] to transition metal oxides such as Cu, Ni, Zn, Cr, and Ce [8, 10, 15, 19]. Noble metals often demonstrate superior activity and selectivity, yet their large-scale deployment is constrained by high cost and susceptibility to poisoning [16]. By contrast, transition metal oxides, and particularly copper-based

systems, have attracted widespread attention due to their abundance, lower cost, and stable catalytic performance [17–18]. Copper catalysts are not only central to ethanol dehydrogenation but also to processes such as methanol synthesis, hydrogenation of carbon oxides, and selective hydrogenation of organic compounds [19–20]. Their activity is strongly governed by the interaction of copper with supports and other oxides, with the incorporation of Zn, Cr, or Ce modifying structural, electronic, and acid–base properties, thereby influencing catalytic performance [21–22].

Among these systems, ZnO–CuO binary catalysts are of particular interest, combining the redox functionality of copper with the acid–base properties of zinc oxide [23]. This synergy has been well established in methanol synthesis from syngas, where the interplay between ZnO and Cu nanoparticles determines catalytic efficiency [24]. It is hypothesized that analogous cooperative effects may enhance ethanol dehydrogenation, leading to improved acetaldehyde selectivity and greater catalyst stability [25–26]. Previous studies have emphasized that Zn/Cu ratio, synthesis method, and calcination conditions significantly affect phase composition, crystallinity, and textural properties [25]. For example, increasing Zn content promotes ZnO-rich phases, altering CuO dispersion and modifying ethanol conversion pathways [27]. The surface acidity and basicity, crucial factors in competing side reactions such as dehydration to ethylene or esterification to ethyl acetate, can likewise be tuned by controlling the ZnO/CuO ratio [24].

Despite extensive research, the structure–activity relationship of Zn–Cu–O binary oxide catalysts in ethanol dehydrogenation remains insufficiently understood. In particular, systematic correlations linking specific surface area, crystallinity, and phase composition with catalytic performance are limited [24]. Addressing these gaps is critical for the rational design of efficient and selective catalysts for bioethanol upgrading.

The objective of this work is to investigate ethanol dehydrogenation over Zn–Cu–O binary oxide catalysts with varying Zn/Cu atomic ratios. Special attention is devoted to the influence of catalyst composition, phase structure, and specific surface area on activity and product selectivity. Furthermore, the acid–base properties of the catalysts were probed via butene-1 isomerization, offering complementary insight into the role of surface functionality in governing catalytic behavior. Our previous studies have demonstrated that ethanol readily transforms into acetone and acetic acid over Zn–Cu–O systems, with catalytic performance strongly determined by phase composition and crystallinity. These findings suggest that crystallinity, dictated by both precursor choice and synthesis conditions, represents a critical parameter in controlling catalytic efficiency.

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II. Experimental section

Various compositions of binary zinc-copper oxide catalysts were synthesized via the co-precipitation method using aqueous suspensions of zinc carbonate ($ZnCO_3$) and copper (II) nitrate ($Cu(NO_3)_2$) [24]. The obtained mixture was first evaporated and dried at 373 – 393K, after which nitrogen oxides fully decomposed within the range of 523–523 K. Subsequent calcination at 823K for 10 hours yielded the catalysts with Zn:Cu atomic ratios varying from 1:9 to 9:1."

The activity of the synthesized catalysts in the ethanol dehydrogenation and butene-1 isomerization reactions was evaluated using a flow-type fixed bed quartz reactor within the temperature range of 423–723K. To test for ethanol dehydrogenation, 5 ml of the catalyst (1.0–2.0 mm particles) was loaded into the reactor. The reaction rate remained unchanged despite variations in feed rate and particle size (0.5–5 mm), confirming that the process was free from both internal and external diffusion limitations.

In a controlled environment, ethanol dehydrogenation was performed by introducing a steady stream of nitrogen gas into the reactor. The primary function of the nitrogen was to act as a carrier gas and to maintain an oxygen-free environment, ensuring that the observed products resulted solely from the dehydrogenation catalysis. The quantitative analysis of ethanol and all resultant volatile compounds from its conversion was performed using gas chromatography (GC). This

technique was selected for its high resolution and sensitivity, enabling the precise separation, identification, and quantification of the complex mixture of products, which typically includes acetaldehyde, ethyl acetate, butanol, and unreacted ethanol. To determine the crystallographic structure and phase composition of the Zn-Cu oxide catalysts, X-ray diffraction (XRD) patterns were acquired using a Bruker D2 Phaser diffractometer. The instrument was operated with CuKα radiation, a Ni filter to remove the Kβ line, and a scanning interval of $3° \leq 2\theta \leq 80°$. [25].

Additionally, equilibrium constants were determined for ethanol and acetaldehyde conversion yields. The equilibrium constant and Gibbs energy values for the ethanol-to-acetaldehyde dehydrogenation reaction are presented in Table 1.

Table 1: Equilibrium constant and Hibbs energy of the dehydrogenation reaction of ethanol to acetaldehyde at different temperatures

Temperature, K	400	500	600	700	800	900	1000
ΔG, kC/mol	23,21	11,27	-0,887	-13,18	-25,56	-37,99	-50,45
K_t	9,28E-04	6,64E-02	1,19E+0	9,64E+0	4,67E+01	1,61E+02	4,33E+02

The values of Gibbs free energy (ΔG) presented in Table 1 demonstrate the strong influence of temperature on the reaction's spontaneity. The progression of ΔG from a positive value of 23.21 kJ/mol at 400 K to a strongly negative value of -50.45 kJ/mol at 1000 K indicates that the reaction, which is not thermodynamically favorable at low temperatures, becomes strongly favored as temperature increases. The thermodynamic possible yields of acetaldehyde are presented in Figure 1. As the data in figure 1 indicate, with the increase of the reaction temperature, the yield of acetic aldehyde increases sharply starting from 400K and is practically 100% at 700K.

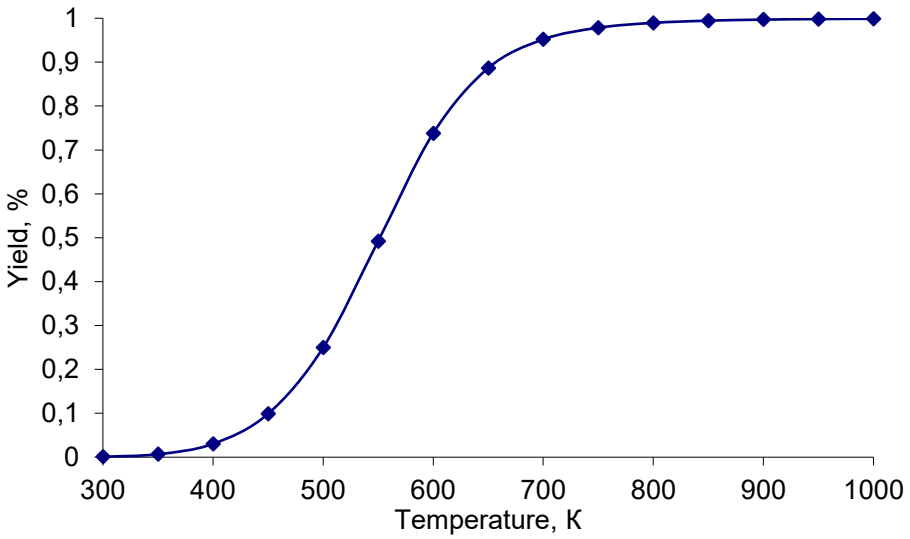

Fig. 1: Dependence of the thermodynamically possible yield of acetic aldehyde on the reaction temperature

According to the scientific literature, one of the properties that reflect the activity of catalysts is that their surface has an acid-based property [6, 13]. The acid-base characterization of heterogeneous catalyst surfaces can be accomplished through numerous analytical techniques. Among these, the assessment of catalytic performance in model reactions provides a direct probe of active site functionality [28]. The isomerization of butene-1 to butene-2 is a well-established model reaction for this purpose, as its mechanism is highly sensitive to the nature and strength of surface acid and base sites. Consequently, to elucidate the acid-base properties of the synthesized binary

zinc-copper oxide (Zn-Cu-O) catalysts, their activity and selectivity were evaluated in the butene-1 isomerization reaction.

The catalytic isomerization of butene-1 to butene-2 was investigated over a temperature range of 423 to 673 K. The reaction was performed under a high gas hourly space velocity (GHSV) of 1200 h^{-1} to ensure the reactor operated in a differential mode, thereby minimizing conversion to accurately determine the intrinsic reaction kinetics and initial product distribution attributable to the catalyst's acid-base properties.

The catalytic performance of the synthesized binary zinc-copper oxide (Zn-Cu-O) systems for the model reaction of butene-1 isomerization to butene-2 is quantitatively summarized in Table 2. The data presented include key metrics such as conversion, selectivity towards butene-2, and cis/trans ratio, which serve as critical indicators of the surface acid-base property balance.

Table 2: Catalytic activity of zinc–copper oxides in the isomerization of butene-1.

Zn-Cu atomic ratio	Temperature, K	Yield, %			Trans/cis ratio
		Trans-	Cis-	Trans+cis sum	
1-9	473	2,5	4,7	7,2	0,53
	523	3,6	7,5	11,1	0,48
	573	4,1	8,4	12,5	0,48
	623	3,3	4,6	7,9	0,72
2-8	473	1,8	3,6	5,4	0,5
	523	2,8	5,4	8,2	0,51
	573	3,6	7,5	11,1	0,48
	623	3	6,2	9,2	0,48
3-7	473	1,2	3,3	4,5	0,36
	523	1,9	4,1	6	0,46
	573	3,7	7,1	10,8	0,52
	623	3,5	5,7	9,2	0,61
4-6	473	1,6	2,7	4,3	0,59
	523	1,7	2,9	4,6	0,58
	573	2,7	6,3	9	0,42
	623	3	11,6	14,6	0,25
5:5	473	0,6	1,8	2,4	0,33
	523	1,3	2,8	4,1	0,46
	573	1,8	5,7	7,5	0,31
	623	3,2	7,1	10,3	0,45
6-4	473	0,5	1,4	1,9	0,35
	523	0,9	1,9	2,8	0,47
	573	1,5	3,2	4,7	0,46
	623	1,7	4,4	6,1	0,38
7-3	473	0,4	1,3	1,7	0,30
	523	0,7	1,6	2,3	0,43
	573	1,1	2,1	3,2	0,52
	623	1,3	2,5	3,8	0,52
8-2	473	0	0,4	0,4	0
	523	0,3	1,2	1,5	0,25
	573	0,9	1,7	2,6	0,52
	623	1	1,9	2,9	0,52
9-1	473	0	0,2	0,2	0
	523	0,2	0,4	0,6	0,5
	573	0,3	0,5	0,8	0,6
	623	0,3	0,7	1	0,42

The catalytic data presented in Table 2 reveal a distinct structure-activity relationship for the butene-1 isomerization reaction over the binary zinc-copper oxide catalysts. Analysis of the Zn-Cu=1-9 catalyst demonstrates that the reaction initiates at a temperature of 473 K, evidenced by the formation of 2.5% trans-butene-2 and 4.7% cis-butene-2. The yield of butene-2 exhibits a pronounced volcanic dependence on temperature, initially increasing with thermal energy to a maximum of 12.5% at 573K. This positive trend is attributed to enhanced activation of reactant molecules on the catalyst's acid-base sites. However, a further temperature increase to 673 K leads to a significant decrease in yield to 6.1%, suggesting the onset of thermal deactivation, competitive side reactions, or possible catalyst sintering.

This yield profile, characterized by an optimum temperature, is a consistent feature across all tested catalysts, with maximum butene-2 yields never exceeding 14.6%. Furthermore, the product distribution, specifically the trans/cis-butene-2 ratio, which fluctuates within a narrow range of 0.33 to 0.72, provides critical insight into the nature of the active sites and the reaction mechanism, potentially favoring a particular adsorption geometry or intermediate. Most significantly, the data conclusively show that the efficacy of the isomerization process is not solely temperature-dependent but is intrinsically governed by the zinc-to-copper (Zn:Cu) atomic ratio within the catalyst structure. This strong correlation indicates that the synergistic interaction between these two metals dictates the population, strength, and balance of the surface acid-base pairs necessary for the reaction, ultimately defining the catalytic performance.

The product distribution of the butene-1 isomerization reaction is strongly influenced by the catalyst's composition. Figure 2 demonstrates this structure-property relationship by correlating the Zn/Cu atomic ratio in the Zn-Cu-O system with the resulting yields of trans- and cis-butene-2 at 523 K. The distinct trends for each isomer suggest that the surface geometry and the acid-base strength pair distribution are directly tunable by the elemental composition.

As can be seen from the Figure 2, increasing the amount of zinc in the catalysts leads to a reduction in the output of trans- and cis-butene-2. Thus, the yield of butene-2 is 11.1% in the Zn-Cu=1-9 sample, and 0.6% in the Zn-Cu=9-1 catalyst. Additionally, at the temperature of 623°C, another dependence is observed.

The catalytic conversion of ethanol over the synthesized zinc-copper oxide (Zn-Cu-O) catalysts was investigated, revealing a complex product distribution indicative of multiple parallel and sequential reaction pathways. The analytical results conclusively identify acetaldehyde (also known as acetic aldehyde) as the principal primary product, originating from the dehydrogenation of ethanol. Secondary products detected include ethylene, carbon dioxide (CO_2), and carbon monoxide (CO), whose formation suggests concomitant dehydration and decomposition/dehydrogenation reactions occurring on the catalyst surface.

A strong correlation between catalytic performance and the metal ratio was observed. As illustrated in the figure, the catalyst with a Zn:Cu atomic ratio of 1:9 exhibits the highest selectivity towards acetaldehyde formation. Intriguingly, a significant divergence in product distribution was noted for the Zn-Cu=2:8 catalyst, which yielded a substantial 43.2% of acetone, indicating a pronounced shift in mechanism likely favoring a concerted dehydrogenation and ketonization pathway. Analysis of the temperature-dependent reactivity profiles indicates that the ethanol dehydrogenation process initiates at a relatively low temperature of 423 K. At this threshold, the reaction is highly selective, producing only acetaldehyde at a yield of 9.9%. This confirms that dehydrogenation is the primary low-temperature pathway. As the temperature is increased, the activation of secondary reactions leads to a more diverse product slate. The yield of acetaldehyde itself demonstrates a dependence on temperature, increasing to a maximum of 41.6% at 573 K before presumably declining at higher temperatures due to further decomposition or side reactions.

The product distribution evolution with temperature reveals distinct activation thresholds for secondary reaction pathways. The formation of ethylene, acetone, and carbon dioxide (CO_2) commences at a temperature of 523 K, indicating the point at which the thermal energy is sufficient

to activate dehydration and ketonization/decomposition mechanisms alongside the primary dehydrogenation pathway.

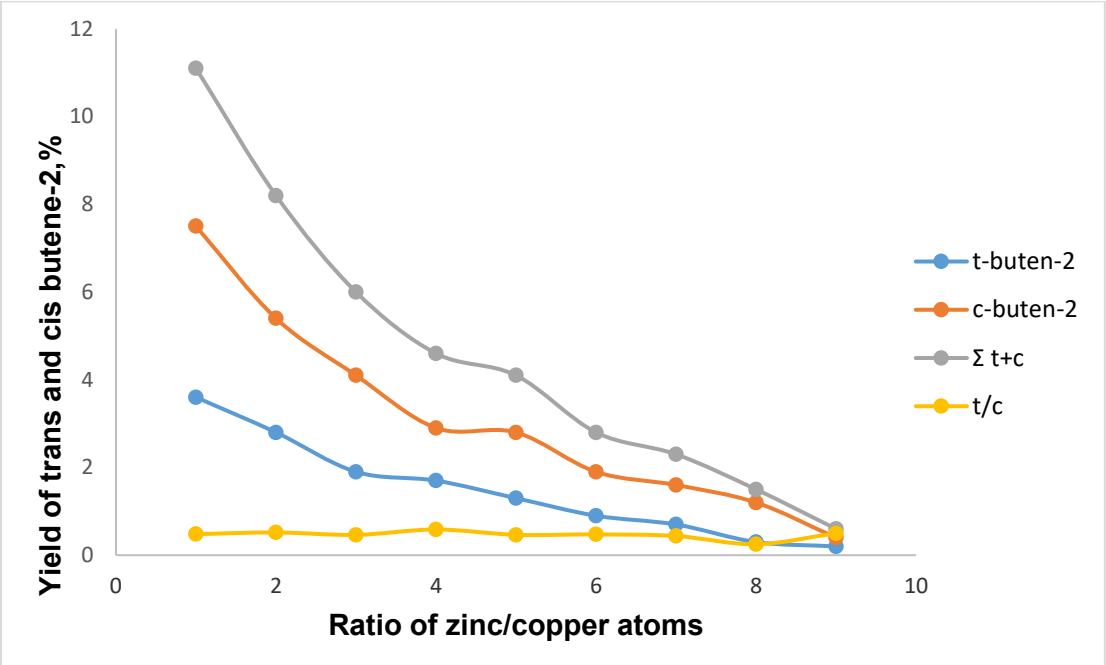

Fig. 2: Variation in the yield of trans- and cis-butene-2 as a function of the Zn-to-Cu atomic ratio in Zn–Cu–O catalysts, T=523°C

As comprehensively detailed in Figure 3, a subsequent increase in reaction temperature significantly alters the product slate. Most notably, the yield of acetaldehyde (acetic aldehyde) exhibits a pronounced decline. This decrease in the primary product is inversely correlated with a rise in the formation of ethylene and acetone, suggesting these species are formed either in parallel or sequential reactions that become thermodynamically and kinetically favored at higher temperatures. This trade-off between products is most extreme for the catalyst with a Zn-Cu atomic ratio of 5:5. For this specific composition, the acetaldehyde yield reaches a minimum, while the production of carbon dioxide is maximized. The Zn-Cu=1:1 catalyst favors deep oxidation to CO_2, reducing acetaldehyde yield.

Initial findings strongly suggested that the Zn/Cu atomic ratio is a pivotal factor governing the activity of zinc-copper oxide catalysts in ethanol dehydrogenation. To explore this further, we conducted a detailed investigation into how the catalyst's composition affects its overall performance. The product distribution—encompassing acetaldehyde, ethyl acetate, acetone, ethylene, and carbon oxides—along with the degree of ethanol conversion, was measured for each catalyst at 573K. These results, which directly demonstrate the composition-activity relationship, are presented in figure 3.

The data presented in Table 3 reveals a clear and significant correlation between the zinc content of the catalyst and the resulting product distribution. Specifically, the yield of acetaldehyde exhibited a substantial positive dependence on zinc loading, increasing dramatically from 9.6% for the zinc-poor catalyst (Zn:Cu = 1:9) to 38.4% for the zinc-rich formulation (Zn:Cu = 9:1). Conversely, the production of ethylene was maximized (25.0%) at the highest zinc concentration. Other products observed included acetone (12.5%) and ethyl acetate (2.2%). Most notably, the data demonstrates that elevating the zinc content drives the reaction selectivity almost exclusively toward acetaldehyde, approaching 100%. Across the entire series of tested catalysts, a high ethanol

conversion of 63.2% was achieved, indicating that the compositional changes primarily influenced product selectivity rather than overall activity.

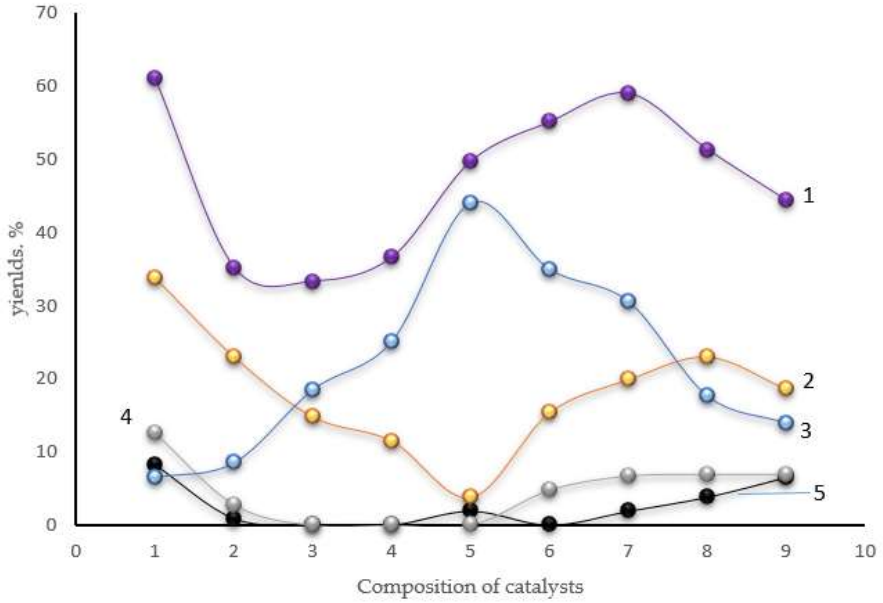

Fig. 3: Effect of temperature on yield of products in ethanol dehydrogenation reaction on Zn:Cu=1:9 catalyst, 1-conversion, 2-CH_3CHO, 3-CO_2, 4-CH_3COCH_3, 5-C_2H_4.

This study establishes acetaldehyde as the primary product of ethanol dehydrogenation using Zn-Cu-O catalysts. The reaction's efficiency and product distribution are highly sensitive to both the reaction temperature and the catalyst's Zn/Cu atomic ratio, underscoring the need for precise control of these variables to maximize target yield and selectivity.

Table 3: Dependence of reaction product yields on temperature (zinc to copper atomic ratio=1:9)

Temperature, K	Yields, %					Conversion, %
	Acetaldehyde	Ethylene	Ethyl acetate	Acetone	CO_x	
423	9.6	-	-	-	-	9.6
473	16.6	-	-	-	-	16.6
523	26.9	-	-	-	-	26.9
573	38.4	3.4	-	2.9	2.9	47.6
623	33.8	8.2	-	12.5	6.5	61
673	28.7	3.9	2.2	11.5	16.4	62.7
723	25.6	10.9	1.1	9.6	25	63.2

It is well-established within catalysis science that the phase composition of a material is a critical determinant of its catalytic activity. This composition, along with other influential structural properties such as crystallinity, is inherently dictated by the precursor compounds and the specific synthesis conditions employed during catalyst preparation (e.g., calcination temperature, pH, and precipitation rate). To investigate this structure-activity relationship within the Zn-Cu-O system, the crystallinity of the synthesized catalysts was systematically correlated with their performance in the ethanol dehydrogenation reaction. X-ray diffraction (XRD) analysis confirmed the presence of two dominant oxide phases within these catalysts. The crystallographic parameters for these identified phases, including lattice constants and space groups, are detailed in Table 4.

Table 4: Crystallographic characteristics of the phases formed in the Zn-Cu-O catalytic system

Chemical combination	Syngonia	Volume group	Network settings				Z, number of molecules
			a, Å	в, Å	c, Å	angle,	
CuO	monoclinic	Cc	4.692	3.428	5.137	99.54	4
ZnO	Rhombic	$Rc\bar{3}$	4.960	-	13.59	-	6

Figure 4 presents the consolidated X-ray diffraction (XRD) patterns for the entire series of nine catalysts, synthesized with varying zinc-to-copper molar ratios (mZn / nCu).

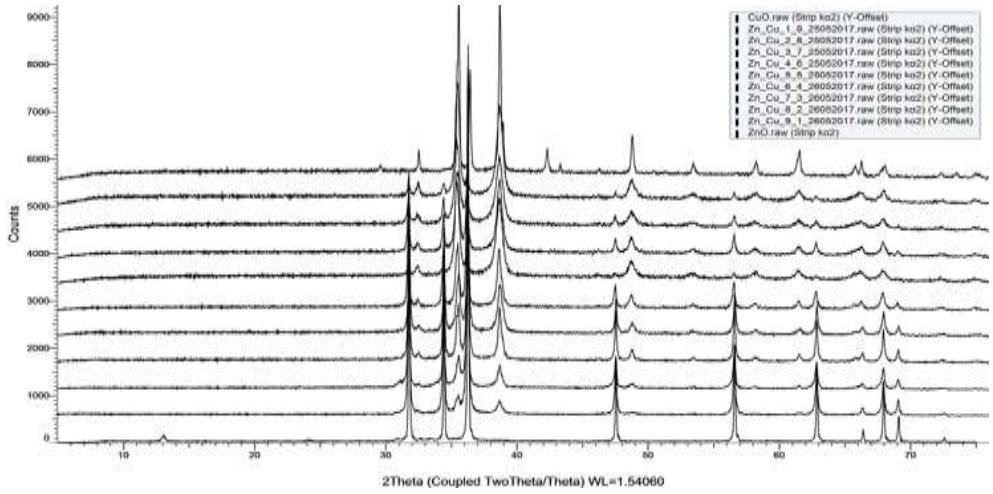

Fig. 4: Diffractograms of zinc and copper oxide as well as Zn-Cu-O catalysts for all nine ratios.

For reference, the standard diffraction patterns for pure zinc oxide (ZnO) and copper oxide (CuO) are included at the top and bottom of the figure, respectively. A thorough analysis of the diffractograms confirms the consistent presence of two distinct crystalline phases across all synthesized samples. Furthermore, a systematic and regular variation in the intensity of the characteristic diffraction peaks is observed across the series. This trend provides clear evidence that the relative ratio of the two phases changes progressively and predictably with the initial mZn /nCu stoichiometry, indicating that the phase composition of the catalysts is directly controllable through the synthesis parameters.

During the conducted research, the crystallinity degrees of all phases were calculated in D2 Phaser using the DIFFRAC.EVA program. The obtained results are shown in table 5. The data presented in the table reveals a strong positive correlation between the zinc content and the degree of crystallinity within the Zn-Cu-O catalytic system. Quantitatively, the crystallinity exhibits a substantial increase, rising from 43.7% for the most zinc-deficient formulation to 93.2% for the sample with the highest zinc concentration. This pronounced enhancement suggests that zinc acts as a crystallizing agent, promoting the formation of a more ordered and well-defined crystalline structure during catalyst synthesis. This evolution in structural order is likely a critical factor influencing the catalytic activity.

Figure 5 presents the relationship between the degree of crystallinity of Zn–Cu–O catalysts and the product distribution in ethanol dehydrogenation, including acetaldehyde, ethyl acetate, acetone, ethylene, and carbon dioxide. The data reveal that with increasing crystallinity, ethanol conversion and carbon dioxide yield exhibit a symmetrical variation, while both the yield and selectivity of acetaldehyde pass through a minimum. Notably, a higher degree of crystallinity ultimately

enhances the selectivity of the reaction toward acetaldehyde formation, underscoring the critical role of structural ordering in governing catalytic performance.

Table 5: Crystallinity level of the Zn–Cu–O system.

Zn-Cu-O system, %	
Zn:Cu atomic ratio	Crystallinity
1:9	42.9
2:8	43.9
3;7	54.9
4:6	44.2
5:5	71.3
6:4	75.3
7:3	78.1
8:2	81.3
9:1	93.8

From the conducted studies, it appears that with the increase in the degree of crystallinity, the release of carbon dioxide exceeds the maximum, while the release of acetaldehyde and the selectivity for acetaldehyde exceed the minimum. The enhancement in the degree of crystallinity cause to an increase in the selectivity of the process for acetaldehyde.

A foundational principle of heterogeneous catalysis is that the transformation of reactants into products occurs exclusively at the catalyst's surface. Consequently, the physicochemical properties of this surface are paramount in determining catalytic activity, with the specific surface area being a primary factor. For complex multi-element catalysts, such as the Zn-Cu-O system, the specific surface area is not an intrinsic property but is critically dependent on synthetic parameters.

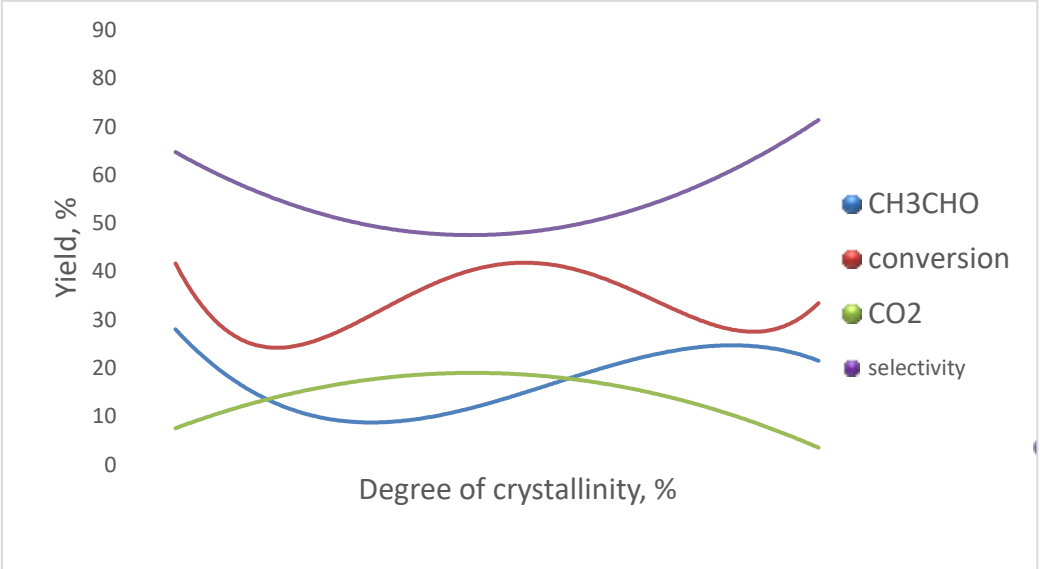

Fig. 5: nfluence of catalyst crystallinity on the activity of Zn–Cu–O in ethanol dehydrogenation at 523 K

Specifically, it is governed by the stoichiometric atomic ratios of the precursor elements and the specific conditions of the preparation methodology (e.g., calcination temperature, precipitation rate, and aging time), which collectively influence nucleation, growth, and ultimately, the final textural properties of the material.

Table 6: Specific surface area of Zn-Cu-O catalysts, m^2/g

Zn/Cu ratio	ZnO	1-9	2-8	3-7	4-6	5-5	6-4	7-3	8-2	9-1	CuO
S, m^2/g	4.0	8,0	3,5	4,3	5,6	6,5	6,0	4,7	5,5	4,7	0,6

The table shows the obtained values of the specific surface area of the samples of the Zn-Cu-O catalytic system by the nitrogen thermal desorption method. As can be seen from the table, the value of the specific surface increases with the increase of the amount of zinc in the samples except for the Zn-Cu=1-9 catalyst for the zinc-copper oxide catalytic system, while the specific surface in the sample containing Zn-Cu=5-5 passes through the maximum and then decreases. The specific surface area in the Zn-Cu=9:1 catalyst is 4.7 m2/g. The obtained results show that the specific surface area of the samples in the Zn-Cu-O system varies between 3.5 m2/g (Zn-Cu=2-8) and 8.0 m2/g (Zn-Cu =1:9). The value of primary oxides, i.e. zinc and copper oxides, is 4.0 and 0.6 m2/g, respectively.

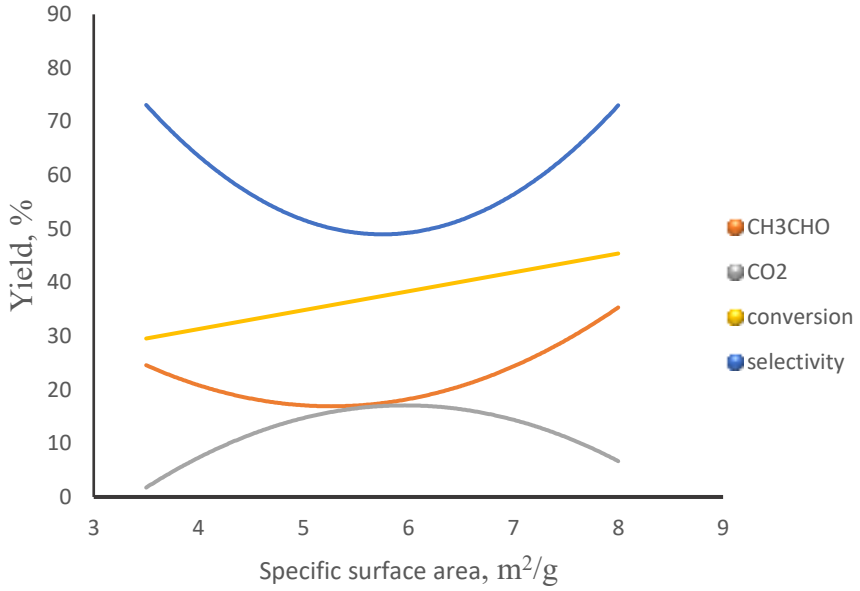

Fig. 6: Effect of specific surface area on the activity of Zn-Cu-O catalysts in ethanol dehydrogenation reaction. T=573K

Figure 6 illustrates the correlation between the specific surface area of Zn-Cu-O catalysts and the product distribution from ethanol dehydrogenation. The data reveals a clear positive relationship between ethanol conversion and the catalyst's specific surface area; as the surface area increases, so does the conversion. However, this enhancement in activity is accompanied by a shift in selectivity. While acetaldehyde remains the principal reaction product, its selectivity reaches a minimum at higher surface areas. Concurrently, the yield of carbon dioxide is maximized under these conditions.

This behavior can be explained by considering the catalyst's phase composition. Samples with a high specific surface area are typically associated with non-stoichiometric formulations where one element is in excess, leading to the formation of solid solutions. These specific structural features appear to promote secondary reactions, such as decomposition or oxidation, that consume acetaldehyde and generate CO_2. In contrast, catalysts with a lower surface area, often comprising a simple mixture of primary ZnO and CuO phases due to a more balanced stoichiometry (e.g., 1:1 ratio), favor the selective dehydrogenation pathway to acetaldehyde.

This study establishes that the specific surface area of Zn-Cu-O catalysts has a distinct effect on ethanol dehydrogenation. Analysis of the data reveals an inverse correlation between surface area and acetaldehyde yield; as the surface area increases, the yield of the target product, acetaldehyde, falls to a minimum. This indicates that maximizing surface area is not an optimal strategy for this particular catalytic system, as it promotes non-selective reaction pathways.

III. Conclusion

Catalytic dehydrogenation of ethanol over zinc–copper oxide (Zn–Cu–O) catalysts proceeds with high selectivity, yielding acetaldehyde as the principal product. Structural characterization via X-ray diffraction (XRD) confirmed that the catalytic system comprises distinct ZnO and CuO phases, with no evidence of extensive solid solution formation. Importantly, the coexistence of these phases reflects a synergistic interplay between redox-active copper species and the acid–base functionality of zinc oxide, which underpins both catalytic reliability and environmental compatibility of the process.

A strong structure–activity relationship was elucidated, wherein the catalyst's performance is critically dependent on its physicochemical properties. Specifically, an increase in the degree of crystallinity was found to enhance both the acetaldehyde yield and the process selectivity toward this desired product. This suggests that crystallinity can serve as a predictive marker of catalytic reliability, ensuring reproducible performance across different synthesis batches. Conversely, the specific surface area (SSA) of the catalyst was identified as a key parameter exerting a significant, yet complex, influence on the reaction outcome. The yield of acetaldehyde was observed to be highly sensitive to variations in SSA, indicating a non-linear relationship that merits further investigation and long-term monitoring to guarantee process stability under industrial conditions.

Furthermore, the catalytic functionality of the binary Zn–Cu–O system was extended to the isomerization of butene-1. The composition of the catalyst was determined to be a decisive factor, with the yields of the isomerization products, trans-butene-2 and cis-butene-2, reaching a maximum at a specific optimal zinc-to-copper ratio of 4:6. This demonstrates a pronounced compositional dependence for activity in this complementary reaction and highlights the broader versatility of Zn–Cu–O systems as multifunctional, reliable, and eco-sustainable catalysts. By linking phase composition, crystallinity, and surface area to catalytic behavior, this study provides new insights into how structural parameters can guide the rational design of durable catalysts that simultaneously meet performance and environmental sustainability targets.

CONFLICT OF INTEREST

Authors declare that they do not have any conflict of interest.

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