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Structure–activity relationships of Cu–La–O catalysts in ethanol dehydrogenation

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The catalytic performance of Cu–La–O mixed oxides in the ethanol dehydrogenation process is governed by the interplay between crystalline structure, surface basicity, and Cu–O–La interfacial sites. The Cu:La = 6:4 composition provides optimal nanoparticle dispersion, mesoporosity, and acetaldehyde selectivity. The structural characteristics and catalytic performance of Cu–La–O mixed oxide catalysts in the dehydrogenation reaction of ethanol to acetaldehyde were systematically investigated. Cu–La–O catalysts with different Cu:La molar ratios (8:2, 7:3, 6:4, and 5:5) were synthesized via co-precipitation and calcined at 450–500 °C. X-ray diffraction data confirmed the presence of CuO and La_2O_3 phases, with a Cu:La = 6:4 composition promoting highly dispersed CuO nanoparticles. BET analysis revealed that this ratio provided the highest specific surface area (61 m^2/g). The pore volume (0.29 cm^3/g) calculated from the adsorption–desorption isotherms using the BJH method, indicates the formation of a well-developed mesoporous structure. Catalytic tests demonstrated that the ratio Cu:La = 6:4 provided the highest ethanol conversion (85%) and acetaldehyde selectivity (97%), while excess La_2O_3 (5:5) partially blocked active sites, reducing performance. The enhanced catalytic activity is attributed to the formation of Cu–O–La interfacial sites, optimizing redox properties and surface basicity. These findings provide insight into the structure–activity relationships of Cu–La–O catalysts and guidance for designing selective, stable, and energy-efficient catalysts for acetaldehyde production.

Keywords: Acetaldehyde; ethanol dehydrogenation; Cu–La–O mixed oxides; structure–activity relationship; BET surface area; X-ray diffraction

Співвідношення між структурою та активністю каталізаторів Cu–La–O в дегідрогенуванні етанолу. *Selime Mammadova[a], Aytan Abdullayeva[b], Vilayet Mammadov[c], Ikhtiyar Bakhtiyarly[c], Ziyafat Muxtarova[c]*

Каталітична продуктивність змішаних оксидів Cu–La–O в реакції дегідрування етанолу визначається взаємодією між кристалічною структурою, основністю поверхні та міжфазними ділянками Cu–O–La. Співвідношення Cu:La = 6:4 забезпечує оптимальну дисперсію наночастинок, мезопористість та селективність ацетальдегіду. Систематично досліджені структурні характеристики та каталітична продуктивність каталізаторів змішаних оксидів Cu–La–O в реакції дегідрування етанолу до ацетальдегіду. Каталізатори Cu–La–O з різними молярними співвідношеннями Cu:La (8:2, 7:3, 6:4 та 5:5) були синтезовані шляхом спільного

осадження та відпалені при 450–500 °C. Рентгенівська дифракція підтвердила наявність фаз CuO та La_2O_3, причому співвідношення Cu:La = 6:4 сприяє утворенню високодисперсних наночастинок CuO. БЕТ-аналіз показав, що це співвідношення забезпечує найвищу питому площу поверхні (61 м²/г). Об'єм пор (0,29 см³/г), розрахований за ізотермами адсорбції-десорбції методом BJH, вказує на формування добре розвиненої мезопористої структури. Каталітичні випробування показали, що при співвідношенні Cu:La = 6:4 досягається найвища конверсія етанолу (85%) та селективність ацетальдегіду (97%), тоді як надлишок La_2O_3 (5:5) частково блокував активні центри, знижуючи продуктивність. Підвищена каталітична активність пояснюється утворенням міжфазних центрів Cu–O–La, що оптимізує окисно-відновні властивості та основність поверхні. Ці результати дають уявлення про взаємозв'язки між структурою та активністю каталізаторів Cu–La–O та дозволяють дати рекомендації щодо розробки селективних, стабільних та енергоефективних каталізаторів для виробництва ацетальдегіду.

1. Introduction

Heterogeneous catalytic dehydrogenation of ethanol is one of the most efficient and environmentally friendly processes widely used for the production of acetaldehyde [1-3]. Acetaldehyde is an important intermediate in the chemical industry and is extensively used in the synthesis of acetic acid, pentaerythritol, heterocyclic compounds, aromatic aldehydes, dyes, polymers, and many other chemicals [1; 4-7]. Catalytic ethanol dehydrogenation is characterized by high selectivity, low energy consumption, and minimal by-product formation. During the reaction, acetaldehyde is the main product, while molecular hydrogen is the only by-product, which makes the process economically attractive and environmentally favorable [8-12].

Copper-based oxide catalysts (CuO, Cu_2O) are among the most widely used catalytic systems for ethanol dehydrogenation [13-15]. This is mainly attributed to the optimal electronic structure of the Cu^{2+}/Cu^{+} redox couple for the activation of O–H and α-C–H bonds in alcohol molecules [16; 17]. The relatively low energy required for hydrogen abstraction on copper oxides results in high selectivity toward acetaldehyde formation [18; 19]. However, sintering of the copper oxide phase at elevated temperatures, particle growth and, as a consequence loss of active centers significantly reduce catalyst stability. Therefore, the use of various oxide promoters to improve the stability and dispersion of Cu-based catalysts has been extensively investigated [20]. The degree of dispersion of the CuO phase can be inferred from the width and intensity of the XRD diffraction peaks, which provide information about the size of CuO crystallites. Peak broadening indicates that the CuO particles are smaller in size and more finely dispersed on the catalyst surface.

Rare earth metal oxides, particularly lanthanum oxide (La_2O_3), have attracted considerable attention in recent years as modifiers for copper catalysts. La_2O_3 exhibits high basicity, enhances oxygen ion mobility, and optimizes the surface acid–base balance [21]. The incorporation of La_2O_3 suppresses the growth of CuO crystallites, promotes the formation of highly dispersed CuO particles, and facilitates the generation of Cu^{+} active sites. These sites are considered the primary catalytic centers for ethanol adsorption and α-C–H bond cleavage. Moreover, oxygen defects and basic O^{2-} sites induced by La_2O_3 improve ethanol adsorption on the catalyst surface and accelerate the reaction rate [22; 23].

In Cu–La–O mixed oxide systems, the formation of Cu–O–La interfacial sites can significantly modify the electronic and structural properties of the catalyst, thereby optimizing the redox behavior of copper species [24]. Such interfaces facilitate the $Cu^{2+} \rightarrow Cu^{+}$ transition, which is a crucial step for the selective formation of acetaldehyde [25]. In addition, the La_2O_3 matrix enhances the thermal stability of the catalyst and suppresses carbon deposition, ensuring long-term catalytic performance [26-29].

Although Cu–La–O catalysts have been investigated for various reactions, a comprehensive understanding of the structure–activity relationships specifically in the ethanol dehydrogenation reaction remains an important and unresolved problem [30-32]. Key issues include the interaction between CuO and La_2O_3 phases, the effect of crystallite size, the formation of Cu^{+} active sites, and the role of surface basicity [33].

In this work, the relationships between the structural–textural properties of Cu–La–O catalysts with different Cu:La molar ratios and their catalytic activity in the ethanol dehydrogenation process were systematically investigated. The aim of this study is to elucidate the effect of Cu–La on the crystalline structure, dispersion, redox behavior, and surface basicity

of the catalysts, and to identify the most optimal catalyst composition. The optimal catalyst composition was determined based on the comparison of ethanol conversion and selectivity toward acetaldehyde. The catalyst with a Cu:La ratio of 6:4 was considered optimal as it demonstrated both high conversion and high selectivity (Table 1).

This research contributes both to a fundamental understanding of Cu–La–O oxide systems and to the practical development of highly selective and more stable catalysts for the synthesis of acetaldehyde.

The dehydrogenation of ethanol proceeds according to the following reaction:

$$C_2H_5OH \rightarrow CH_3CHO + H_2$$

One of the most critical aspects of this reaction is achieving high acetaldehyde selectivity while suppressing carbon deposition processes. In this respect, CuO–La_2O_3 systems are considered particularly promising.

Acetaldehyde (CH_3CHO) is widely used in the production of acetic acid, dyes, polymers, and other chemicals [34]. Among the most efficient methods for acetaldehyde production is the heterogeneous catalytic dehydrogenation of ethanol [35]. This process can be carried out at relatively low temperatures, with high selectivity, and in comparatively simple reactor systems.

2. Materials and methods

2.1. Catalyst preparation

Cu–La–O catalysts were synthesized using the co-precipitation method. During the synthesis, aqueous solutions of $Cu(NO_3)_2 \cdot 3H_2O$ and $La(NO_3)_3 \cdot 6H_2O$ were prepared with different Cu:La molar ratios (8:2, 7:3, 6:4, and 5:5) and completely dissolved in distilled water. A 1 M NaOH solution was added dropwise to the mixed solution while maintaining the pH in the range of 9–10. After the formation of the precipitate, the suspension was continuously stirred for 1 h to ensure homogeneity. The resulting precipitate was washed several times with distilled water, filtered, and dried at 110 °C. Subsequently, the samples were calcined at 450–500 °C for 4 h.

As a result of calcination, catalysts consisting of CuO, La_2O_3, and Cu–La mixed oxide phases were formed. The main advantages of this synthesis method include effective homogeneous mixing of copper and lanthanum species and the formation of nanosized oxide phases.

2.2. Catalyst characterization and catalytic testing

The structural and textural properties of the synthesized Cu–La–O catalysts were characterized using a combination of instrumental techniques [36]. The crystalline structure and phase composition were investigated by X-ray diffraction (XRD). XRD measurements were performed on a Bruker D2 Phaser powder diffractometer using Cu Kα radiation. Analysis of the diffraction patterns allowed identification of the CuO and La_2O_3 phases, their dispersion, crystallite sizes, and degree of crystallinity. Phase identification, crystallinity, and crystallite size were determined from the full width at half maximum (FWHM) of the diffraction peaks. The results confirmed the presence of monoclinic CuO, and it was noted that the addition of La enhanced the dispersion of CuO nanoparticles.

The specific surface area of the catalysts was determined by nitrogen adsorption using the Brunauer–Emmett–Teller (BET) method. Prior to analysis, the samples were degassed in a flow of inert gas, and nitrogen adsorption–desorption isotherms were recorded at liquid nitrogen temperature. Based on these isotherms, the specific surface area was calculated. The pore volume and pore size distribution were determined from the desorption branch using the Barrett–Joyner–Halenda (BJH) method. It was found that the inclusion of La_2O_3 in the catalyst increases the specific surface area, improves the dispersion of CuO nanoparticles and promotes the development of mesoporous structure.

The products of ethanol dehydrogenation were analyzed chromatographically [37; 38]. Carbon monoxide was quantified using a Gazochrom-3101 gas chromatograph equipped with a 2 m column packed with activated carbon. Organic products were analyzed using an LKhM-8MD chromatograph with a flame-ionization detector and a 3 m column packed with Polysorb-1 polymer sorbent. Product yields were calculated from the peak areas in the chromatograms, taking into account correction factors determined via absolute calibration with standard mixtures of known composition. Catalyst activity was expressed as the amount of product formed per unit surface area per unit time (mol/(m² ·h)).

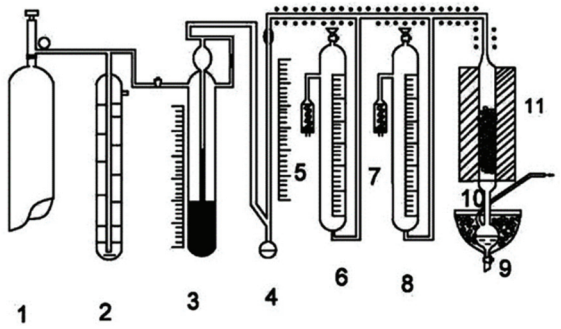

Fig. 1. Experimental setup for studying the catalytic activity in the ethanol dehydrogenation reaction: 1 – nitrogen cylinder; 2 – manostat; 3 – rheometer; 4 – bubble flow meter; 5 – electrolyzer; 6 – feed reservoir; 7 – electrolyzer; 8 – water reservoir; 9 – condenser; 10 – reactor; 11 – furnace.

$$W = \frac{n \cdot \nu_o \cdot \alpha_i}{s \cdot 100} \left[\frac{mmol}{m^2 \cdot s} \right]$$

(where n is the number of moles, ν_0 is the flow rate, α_i is conversion, s is the surface area).

The catalytic activity of the catalysts in the ethanol dehydrogenation reaction was studied using a flow-type laboratory setup with an integral reactor (Fig.1). The catalysts were prepared in the form of tablets using a press, then crushed and sieved. For catalytic testing, 5 g of the catalyst was loaded into the reactor. The particle size of the catalyst ranged from 1 to 2 mm. This procedure was applied to standardize the particle size and ensure homogeneous distribution within the reactor bed, which is important for proper mass and heat transfer control during the reaction.

A mixture of ethanol and nitrogen in a ratio of 1:9 was passed through the catalyst bed. The feed rate of the initial reactants was 1200 h^{-1}. The temperature (150–400 °C) was regulated by a furnace with thermocouple feedback and a voltage stabilizer for uniform heating. The contact time was 3 hours, the experiments were carried out over 3–4 cycles, and the products were analyzed by gas chromatography.

Electrolytic gases (5 and 7) were used to introduce ethanol into the heated inert nitrogen stream, displacing it from the reservoirs (6 and 8). During electrolysis, the generated gases pushed the ethanol–water mixture into a heated tube, where it was vaporized and mixed with the inert nitrogen stream before entering the quartz reactor (11). The ethanol dehydrogenation reaction took place in the reactor. To maintain a stable ethanol feed, a constant voltage was supplied to the electrolyzer using a VSA-ShB type stabilizer.

All reaction products were directed into a condenser, where liquid products were condensed, while gaseous products were analyzed and then released into the atmosphere.

Table 1. Results of ethanol dehydrogenation to acetaldehyde

Cu:La Ratio	Acetaldehyde Selectivity (%)	Ethanol Conversion (%)
Cu:La = 8:2	75	48
Cu:La = 7:3	84	62
Cu:La = 6:4	97	85
Cu:La = 5:5	88	69

3. Results and discussion

The observations indicate that both the catalytic activity and selectivity strongly depend on the Cu:La molar ratio. The catalytic tests were carried out at 150–400 °C using 5 g of catalyst and an ethanol/inert gas mixture. The products were analyzed by gas chromatography. All catalyst samples were used in equal mass to ensure a proper comparison. The catalytic activity was evaluated over 3–4 cycles. The contact time was 3 h. All catalyst samples were tested under identical conditions to ensure a fair comparison. The optimal ratio was determined based on both ethanol conversion and acetaldehyde selectivity.

The catalytic performance of bimetallic Cu–La catalysts with different Cu:La molar ratios (8:2, 7:3, 6:4, and 5:5) was investigated in the dehydrogenation of bioethanol. The results for ethanol conversion and acetaldehyde selectivity are summarized in Table 1.

For the Cu:La = 8:2 catalyst, the ethanol conversion was 48% and the acetaldehyde selectivity was 75%. Increasing the La content to a 7:3 ratio enhanced the conversion to 62% and the selectivity to 84%. The 7:3 ratio improves performance, however, the optimal balance is achieved at Cu:La = 6:4, where the ethanol conversion reached 85% and the acetaldehyde selectivity was 97%. A further increase in the La content (Cu:La = 5:5) led to a decrease in the conversion to 69% and selectivity to 88%.

These results suggest that the Cu–La catalyst with a Cu:La = 6:4 ratio provides an optimal balance between Cu active sites and the La_2O_3 promoter, enhancing the dispersion of

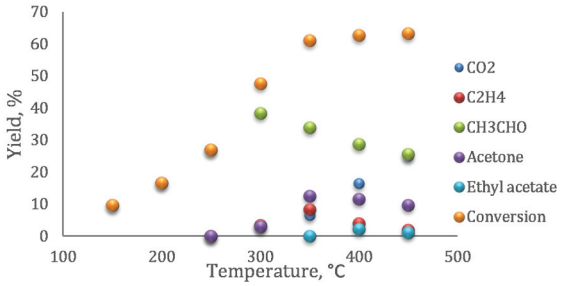

Fig. 2. Investigation of bioethanol dehydrogenation using a bimetallic Cu–La (6:4) catalyst

CuO nanoparticles and facilitating the formation of Cu^+ species, which are crucial for selective acetaldehyde formation. The reduced performance of the catalyst ratio of 5:5 can be attributed to partial coverage of CuO active sites and the formation of fewer active phases.

Figure 2 shows that the product yield depends on temperature, reaching a maximum in the 250-300 °C range. This confirms the optimal operating temperature range for the catalyst.

Figure 3 shows the dependence of the activity of Cu–La–O catalysts on their composition in the ethanol dehydrogenation.

As shown in the figure, at lower temperatures (200–250 °C), the ethanol conversion is relatively low and the formation of by-products such as CO_2 and C_2H_4 is predominant. As the temperature increases up to 300 °C, the yield of acetaldehyde (CH_3CHO) increases sharply, indicating that the dehydrogenation reaction becomes dominant. At higher temperatures (350–400 °C), the acetaldehyde yield decreases, while the formation of ethyl acetate ($C_2H_5OOCCH_3$) and acetic acid (CH_3COOH) increases. This behavior suggests that acetaldehyde undergoes sequential reactions, leading to the formation of secondary products. Meanwhile, the overall ethanol conversion increases with temperature and reaches a maximum at approximately 400 °C.

The results indicate that the optimal operating temperature range for the Cu–La (6:4) catalyst lies between 300 and 350 °C, where the high ethanol conversion and relatively high selectivity toward acetaldehyde are achieved. The presence of La enhances the structural stability of the catalyst, suppresses sintering of the active phase, and helps maintain the effectiveness of Cu active sites.

Figure 4 shows the influence of temperature on the yield of the products of the bioethanol dehydrogenation reaction over the bimetallic Cu–La catalyst with a Cu:La ratio of 8:2.

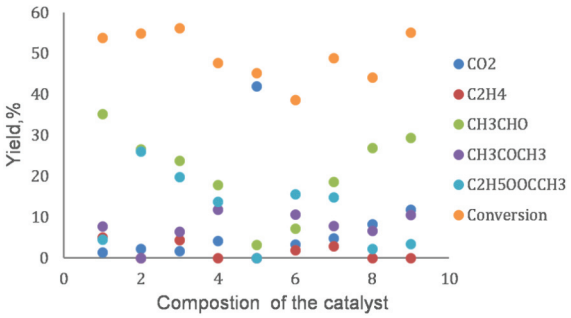

Fig. 3. Dependence of the activity of Cu–La–O catalysts on their composition in the ethanol dehydrogenation reaction at 300 °C

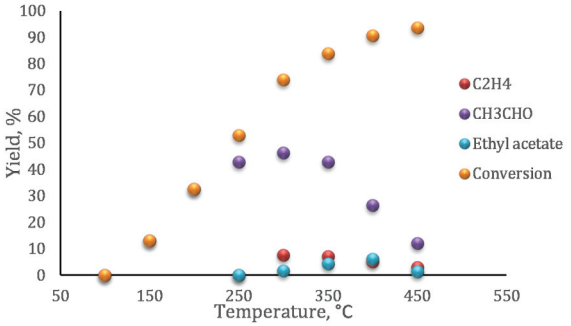

Fig. 4. Effect of reaction temperature on the yield of products from bioethanol dehydrogenation on a bimetallic Cu–La catalyst (Cu:La = 8:2)

According to the analyses conducted, when using catalysts based on lanthanum and copper oxides, ethanol dehydrogenation up to 300 °C predominantly yields ethyl acetate and acetaldehyde, whereas at higher temperatures, ethyl acetate and acetic acid become the predominant products. The dependence of product yields on the catalyst composition exhibits a double-peak behavior, probably associated with the formation of solid solution phases. For the catalyst with a Cu:La ratio of 8:2, the ethanol conversion reaches 48% with an acetaldehyde selectivity of 75%, indicating that Cu is the main active component and La is a stabilizer. As shown in Figure 4, increasing the reaction temperature leads to maxima in the yields of acetaldehyde, ethyl acetate, and ethylene. The ethanol conversion increases steadily over the investigated temperature range, reaching a maximum of 93.5% at 450 °C. A similar temperature dependence was observed for other compositions of La–Cu–O oxide catalysts. Moreover, the catalytic activity of these bimetallic catalysts is significantly influenced by their component ratios and overall composition.

The X-ray diffraction pattern (Fig. 5) shows diffraction peaks corresponding to the hexagonal crystal structure of the Cu/La_2O_3 system.

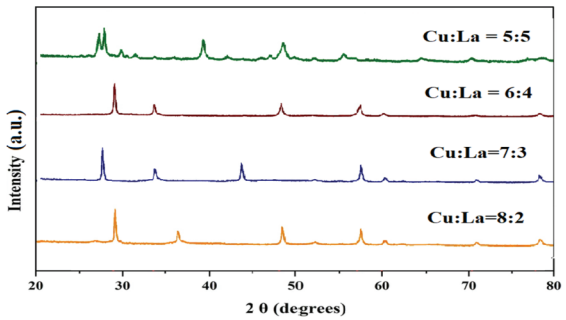

Fig. 5. XRD patterns of Cu-La-O catalysts

The crystallinity of the Cu/La_2O_3 catalyst reached 96.5% at a Cu:La ratio of 6:4, while for 8:2 and 7:3 ratios, it was 69% and 73.3%, respectively. At a 5:5 ratio, the CuO phase is represented by sharper peaks.

1. Cu:La = 5:5 catalyst: The XRD peaks corresponding to CuO and La_2O_3 phases have approximately equal intensity, indicating a relatively uniform distribution of the two phases in the catalyst. The structure is predominantly characteristic of a two-phase system, with weak-to-moderate interactions between the phases.

2. Cu:La = 6:4 catalyst: The intensity of CuO peaks begins to increase, while the relative intensity of La_2O_3 peaks decreases. This suggests an increase in the number of Cu-based active sites, forming a structure more favorable for catalytic activity. This composition is often considered optimal for achieving a highly active catalytic structure.

3. Cu:La = 7:3 catalyst: CuO peaks become sharper and more intense, whereas La_2O_3 peaks weaken. The Cu–La interaction (via Cu–O–La bridges) is strengthened.

4. Cu:La = 8:2 catalyst: The CuO phase becomes fully dominant, with high peak intensities, while La_2O_3 acts primarily as a stabilizer. This composition exhibits high catalytic activity, though long-term stability may be reduced.

The indexing was performed by comparing the experimental data with standard JCPDS cards (No. 45-0937 for CuO and No. 05-0602 for La_2O_3). This confirms the phase purity of the synthesized Cu–La–O catalysts.

Increasing the La_2O_3 content (6:4 and 5:5 ratios) promotes the formation of the CuO phase with higher dispersion. The broadening of the diffraction peaks indicates that the copper oxide phase exists in a nanodispersed state. This high dispersion is critical for catalytic activity, as it generates a greater number of accessible active sites on the catalyst surface.

The crystallinity of the catalysts was evaluated based on the analysis of the intensity of XRD diffraction peaks. The analyses were carried out using a Bruker D2 Phaser diffractometer with CuKα radiation (λ = 0.15406 nm). The diffraction data were processed using the Diffrac.EVA software. The crystallite size was calculated using the Scherrer equation based on the full width at half maximum (FWHM) of the main diffraction peaks. The intensity and width of the peaks provided information about the degree of crystallinity of the catalyst samples and the dispersion of the CuO phase.

For catalysts prepared with different Cu:La molar ratios, the crystallinity values were esti-

Table 2. XRD Peak positions, Miller Indices, and crystal structures of CuO and La_2O_3 Phases

Substance (Phase)	2θ Angle (°)	Miller Index (hkl)	Crystal Structure
CuO (Tenorite)	32.5	(110)	Monoclinic
	35.5	(1□11)	
	38.7	(111)	
	48.7	(2□02)	
	53.7	(020)	
	58.3	(202)	
	61.5	(113)	
	66.2	(311)	
La_2O_3 (Lanthanum oxide)	27.5	(100)	Hexagonal
	29.5	(002)	
	39.5	(101)	
	48.0	(102)	
	56.3	(110)	
	64.8	(103)	

Table 3. Crystallinity of Cu–La–O Catalysts

Cu:La Ratio	Crystallinity (%)
8:2	69
7:3	73.6
6:4	96.5
5:5	57

mated as 69%, 73.6%, 96.5%, and 57% for ratios of 8:2, 7:3, 6:4, and 5:5, respectively.

The results indicate that increasing the La_2O_3 content initially enhances the crystallinity, reaching a maximum of 96.5% at a Cu:La ratio of 6:4. This high crystallinity can be attributed to a more ordered formation of CuO and La_2O_3 phases and the stabilization of the crystal structure through Cu–La interactions, reflecting the optimal organization of the crystalline phase. Further increasing the La content to a 5:5 ratio leads to a decrease in crystallinity to 57%. This reduction is associated with the formation of amorphous regions, increased lattice disorder, and partial destruction of the CuO crystalline phase due to the excessive presence of La_2O_3.

It should be noted that a high degree of crystallinity in the catalyst facilitates the complete conversion of ethanol to acetaldehyde. This indicates that increasing crystallinity in the lanthanum–copper oxide catalysts significantly enhances selectivity toward acetaldehyde formation. Accordingly, for achieving high selectivity in the ethanol-to-acetaldehyde conversion, catalysts should be synthesized with a high degree of crystallinity. As shown in the figure, an increase in the catalyst crystallinity is accompanied by changes in the acetaldehyde yield and the reaction selectivity toward this product. Notably, at a certain level of crystallinity, selectivity toward acetaldehyde reaches a minimum, followed by a subsequent increase with further crystallinity enhancement. This behavior demonstrates that the crystallinity characteristics of the catalyst have a significant impact on the reaction pathways and product distribution.

After the reaction, the catalytic stability results indicate that the structure did not undergo significant changes during the reaction.

BET Surface Area and Pore Structure

The specific surface area of catalysts can be determined using several techniques [24]. In

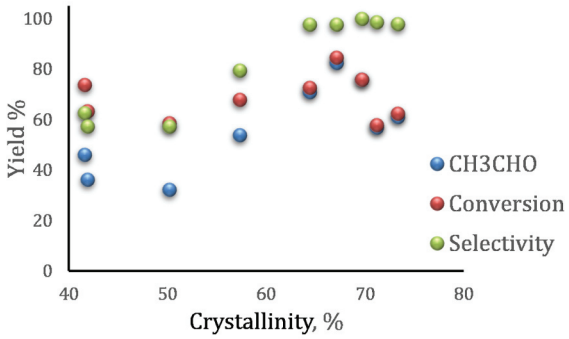

Fig. 6. Effect of crystallinity on the activity of Cu–La-O catalysts in ethanol dehydrogenation

this study, the specific surface area of the catalysts was determined using the BET method. The pore volume and pore diameter were calculated from the desorption branch of the N_2 adsorption–desorption isotherms using the Barrett–Joyner–Halenda (BJH) method. These methods are widely used to characterize the textural properties of mesoporous catalysts. The BET surface area and pore structure were measured using a device based on nitrogen thermal desorption under a helium flow. The sample was exposed to a helium–nitrogen gas mixture and subsequently cooled to liquid nitrogen temperature. The partial pressure of nitrogen in the mixture was adjusted to ensure the formation of a monolayer of adsorbed nitrogen on the catalyst surface during cooling. Upon heating the sample back to room temperature, the adsorbed nitrogen desorbs from the surface and is recorded as a characteristic desorption peak by the instrument. The area of the desorption peak (S_{des}) is related to the amount of desorbed nitrogen and is used for an approximate evaluation of the specific surface area. Accordingly, the catalyst's specific surface area was calculated using the following simplified BET expression:

$$S_{ad.} = \frac{S_{des} \cdot K}{S^0 \cdot q} \quad (m^2/g)$$

The textural properties of the catalysts were determined as follows: BET specific surface area – 31-69 m^2/g; total pore volume – 0.18-0.29 cm^3/g (calculated using the BJH method); pore diameter– 8-14 nm (BJH method); mesopore distribution – 2-50 nm.

It should be noted that this equation represents a simplified, one-point BET calculation and is less accurate than the standard multipoint BET method. These results confirm that the catalysts possess a mesoporous structure.

Table 4. Effect of increasing La content in the Cu:La ratio

Cu/La_2O_3 atom ratio	BET (m^2/g)	pore volume (cm^3/g)	pore diameter (nm)
8:2	32	0.18	14
7:3	45	0.21	11
6:4	**61**	**0.29**	**9**
5:5	58	0.27	8

Table 4 shows that the addition of La up to a Cu:La ratio of 6:4 increases the catalyst's specific surface area, whereas at a 5:5 ratio, partial pore blockage leads to a decrease in surface area. The BET data indicate that the highest surface area is achieved at the 6:4 ratio. Moreover, the reduction in average pore diameter corresponds to the formation of a greater proportion of mesopores. The basicity of the La_2O_3 surface further enhances ethanol adsorption, contributing to improved catalytic performance.

The highest specific surface area was observed for the Cu:La = 6:4 composition. The average pore diameter decreases, leading to an increased proportion of mesopores, while the basicity of the La_2O_3 surface enhances ethanol adsorption. Increasing the La_2O_3 content up to 40% further strengthens the mesoporous structure and maximizes ethanol adsorption.

The textural properties of the catalysts were studied by N_2 adsorption–desorption (BET) analysis. The specific surface area was calculated using the BET method, while pore volume and pore diameter were determined using the BJH method. The analyses were carried out at 77 K. Before measurements, the samples were degassed under vacuum at 250 °C. The specific surface area was calculated using the Brunauer–Emmett–Teller (BET) method, while pore volume and pore diameter were determined using the Barrett–Joyner–Halenda (BJH) method based on the desorption branch. The obtained results indicate that the catalysts possess a mesoporous structure.

The results of BET and BJH analyses for Cu–La–O catalysts show that they have a well-developed mesoporous structure. An increase in the specific surface area leads to a higher number of active sites on the catalyst surface, which enhances catalytic activity in the ethanol dehydrogenation reaction. The pore diameter determined by the BJH method indicates that the porous structure of the catalyst is favorable for the diffusion of reactant molecules to the surface. Larger pore volume and appropriate pore size also facilitate the easy desorption of products from the catalyst surface during the reaction. As a result, these properties enable Cu–La–O catalysts to exhibit high activity and selectivity in the conversion of ethanol to acetaldehyde.

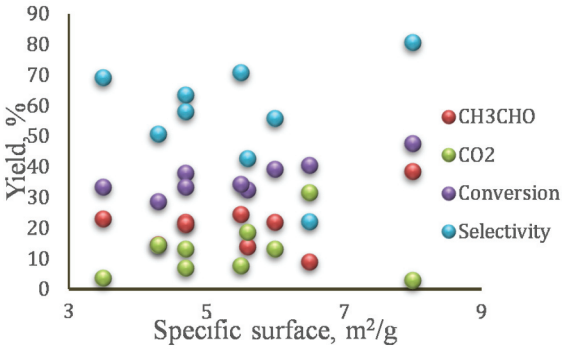

Fig. 7. Effect of specific surface area on the activity of Cu–La-O catalysts in bioethanol dehydrogenation (T = 300°C).

The catalytic activity of catalysts with different Cu:La molar ratios was comparatively investigated in the ethanol dehydrogenation reaction. The results showed that the catalyst with a Cu:La ratio of 6:4 exhibited the highest ethanol conversion and selectivity toward acetaldehyde. This behavior can be explained by a fairly high concentration of active CuO sites and the structural stabilizing effect of the La_2O_3 component. Lanthanum oxide reduces the aggregation of CuO particles, ensuring better dispersion and thereby increasing the active surface area. In addition, La_2O_3 regulates the acid–base properties of the catalyst surface, which positively affects the reaction selectivity. Therefore, the optimal interaction between Cu and La components is observed at a Cu:La ratio of 6:4, making this catalyst the most effective sample for the conversion of ethanol to acetaldehyde.

Figure 7 shows the effect of specific surface area on the catalytic activity of Cu–La–O catalysts in bioethanol dehydrogenation at 300 °C.

Fig. 7 demonstrates that higher surface area correlates with increased catalytic activity.

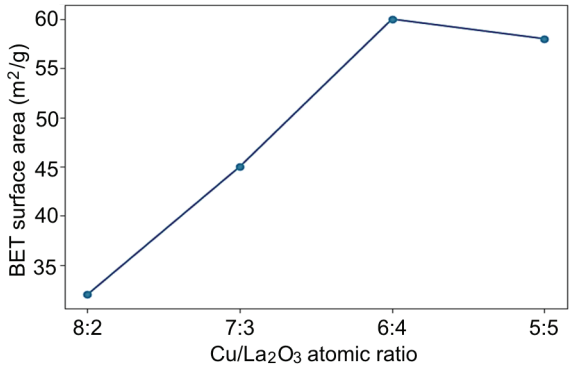

Fig. 8. Effect of Cu:La molar ratio on the BET specific surface area of Cu–La–O catalysts

The Cu:La = 6:4 catalyst possesses the highest surface area (61 m²/g) (Fig. 8), with a pore volume of 0.29 cm³/g (Fig. 9) and an average pore diameter of 9 nm. Increasing the La_2O_3 content (as for the catalysts with 6:4 and 5:5) enhances the mesopore fraction, improving ethanol adsorption. However, for the Cu:La = 5:5 catalyst, partial pore blockage leads to a slight decrease in surface area (58 m²/g) (Fig. 10).

The BET surface area increases with increasing La_2O_3 content from a Cu:La ratio of 8:2 to 6:4, reaching a maximum value of 61 m² g^{-1} for the Cu/La_2O_3 = 6:4 catalyst. A further increase in La_2O_3 content (Cu:La = 5:5) leads to a slight decrease in the surface area due to partial pore blockage caused by excessive La_2O_3, despite improved dispersion of CuO nanoparticles at moderate La_2O_3 loadings.

The pore volume increases with increasing La_2O_3 content from a Cu:La ratio of 8:2 to 6:4, reaching a maximum of 0.29 cm³/g for the Cu/La_2O_3 = 6:4 composition. Further increase in La_2O_3 (Cu:La = 5:5) slightly reduces the pore volume due to partial pore blockage caused by excessive La_2O_3, despite improved CuO nanoparticle dispersion at moderate La_2O_3 loadings.

The pore diameter increases with higher Cu content and decreases with increasing La_2O_3 content. La_2O_3 acts as a structural framework, reducing pore size, whereas Cu-dominant compositions favor larger pores.

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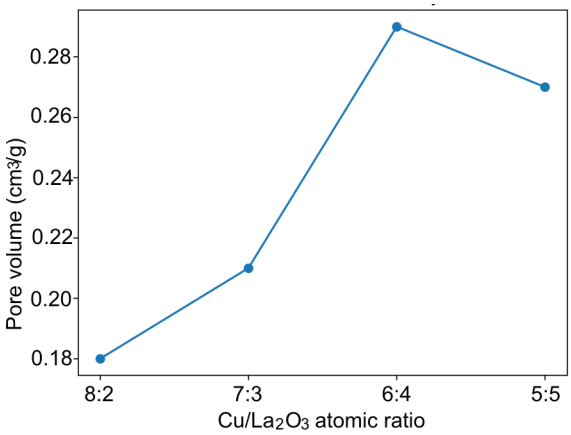

Fig. 9. Effect of Cu:La molar ratio on the pore volume of Cu–La_2O_3 catalysts

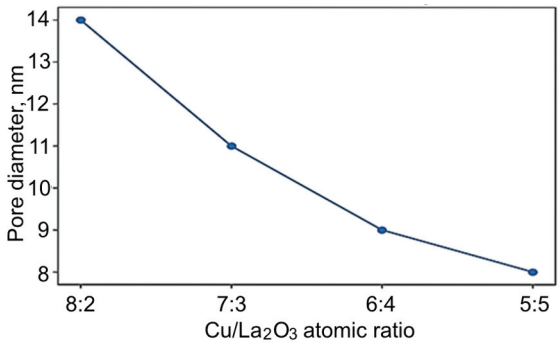

Fig. 10. Effect of Cu:La molar ratio on the pore diameter of Cu–La_2O_3 catalysts

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