

RESEARCH ARTICLE

Syngas production from ethanol dry reforming using $\text{La}_{1-x}\text{K}_x\text{CuO}_3$ perovskite: The effect of potassium promoter

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Abstract - Ethanol dry reforming converts renewable feedstocks and carbon dioxide into valuable syngas, offering a promising pathway for carbon utilization. This study evaluated potassium-promoted lanthanum-copper perovskite catalysts ($\text{La}_{1-x}\text{K}_x\text{CuO}_3$, $x = 0.25 - 1.0$) to modulate product distribution for downstream industrial applications. Synthesized via the citrate sol-gel method, the catalysts were tested in a flow tubular reactor between 973 K and 1073 K and characterized using Fourier transform infrared spectroscopy (FTIR), temperature-programmed reduction (TPR), X-ray diffractometer (XRD), scanning electron microscope with energy-dispersive X-ray spectroscopy (SEM-EDX) and X-ray photoelectron spectroscopy (XPS). Characterization confirmed the successful incorporation of potassium into a single crystalline phase with a linear expansion of lattice parameter for $x \leq 0.50$. Specifically, $\text{La}_{0.50}\text{K}_{0.50}\text{CuO}_3$ exhibited a singular reduction peak at 323°C in H_2 -TPR, reflecting structural homogeneity. XPS verified the oxidation states of surface copper, lanthanum, and potassium species, while SEM-EDX revealed distinct carbon deposition patterns on spent samples. Catalytic results indicated that increasing potassium loading decreased reactant conversions following an exponential decay trend. Nevertheless, potassium modification successfully tailored gas production ratios. All promoted formulations maintained H_2/CO molar ratios above unity, benefiting subsequent synthesis steps. Optimal syngas quality was achieved using the $\text{La}_{0.75}\text{K}_{0.25}\text{CuO}_3$ catalyst, yielding an H_2/CO ratio between 1.5 and 1.6. These findings demonstrate that alkali cation substitution provides a precise control mechanism for syngas stoichiometry in green reforming processes.

Article History

Received : 23 December 2024

Revised : 29 June 2026

Accepted : 29 July 2026

Published : 23 September 2026

Keywords

Ethanol dry reforming

Syngas

Perovskite

Rare earth

Potassium

1. Introduction

Global initiatives to reduce greenhouse gas emissions have accelerated research into renewable energy technologies and sustainable chemical manufacturing. Among carbon utilisation strategies, ethanol dry reforming (EDR) provides a compelling route to transform bio-derived ethanol and carbon dioxide into synthesis gas, a mixture of hydrogen and carbon monoxide, as shown in Eq. (1) [1, 2].



This reaction couple's renewable biomass derivatives with captured CO_2 , supporting circular carbon strategies and green chemistry framework objectives [1, 3]. Ethanol is an ideal liquid reactant because of its high hydrogen ratio, low chemical toxicity, and straightforward production via industrial biomass fermentation. Recent studies show that integrating CO_2 into reforming reactions enhances sustainability by converting greenhouse gases into valuable fuel and chemical intermediates [2, 3]. Syngas derived from EDR serves as a key intermediate for Fischer-Tropsch hydrocarbon synthesis. While industrial syngas relies heavily on fossil fuels, current efforts focus on non-fossil carbon sources to decrease lifecycle carbon emissions.

Despite its thermodynamic advantages, EDR faces operational challenges because it is strongly endothermic, requiring 296.7 kJ/mol of heat at ambient conditions and an activation energy of approximately 97.87 kJ/mol [4]. High-temperature requirements trigger catalyst deactivation via active-metal sintering and carbon accumulation. Side reactions, such as the ethanol thermal decomposition reaction in Eq. (2), deposit filamentous carbon and coke that block active surface sites [2, 5]. Therefore, developing highly stable, coke-resistant catalysts is essential.



Consequently, developing coke-resistant catalytic platforms is critical. Base-metal catalysts (Ni, Co, and Cu) offer cost advantages and good baseline activity, yet they remain vulnerable to rapid coking and particle growth under harsh reaction conditions [6, 7]. Noble metals show superior coke resistance but cost more as raw materials [6]. Perovskite oxides (ABO_3) are versatile catalytic precursors because of their structural robustness, thermal endurance, and adaptable redox capabilities [3, 6]. Partial substitution at the A-site or B-site modulates oxygen vacancy density and metal-support electronic interactions, directly improving carbon resistance and active phase dispersion. Recent advances demonstrate that perovskite-derived catalysts can exhibit strong metal dispersion and enhanced oxygen mobility, which are crucial for inhibiting carbon deposition [5, 6]. Alkaline promoters, particularly potassium, further modify catalyst behaviour by

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increasing surface basicity and facilitating gasification of carbonaceous deposits [1, 7]. Incorporating potassium can suppress methanation reactions, enhance CO₂ activation, and improve coke resistance by increasing the surface mobility of adsorbed species [7]. Therefore, this work aims to investigate the effect of potassium promotion on lanthanum–copper perovskite catalysts (La_{1-x}K_xCuO₃) for ethanol dry reforming, with particular emphasis on catalyst performance and syngas quality.

2. Materials and Methods

This work continued our previous work on the LaCuO₃ catalyst. Thus, the catalyst without potassium (K) promotion can be referred to as Ramkiran et al. [8]. We prepared the catalyst using the same method and tested it in the same EDR setup. The catalyst samples were characterised using infrared and X-ray photoemission spectroscopies, X-ray diffraction (XRD) and scanning electron microscopy, as detailed below.

2.1 Material and Catalyst Preparation

The La_{1-x}K_xCuO₃ perovskite samples were prepared by using the citrate sol-gel method [9, 10] where *x* was varied as 0.25, 0.50, 0.75, and 1 based on mass ratio. We used distilled water to prepare the nitrate solutions. We mixed the nitrate solutions with citric acid and stirred for 5 h at 80 °C until a viscous gel formed. After being filtered, the gel was dried at 120 °C for 24 h in an oven. The solidified gel was ground and sieved to filter coarse from fine powder and estimate particle sizes. Finally, the dried gel was calcined in a furnace at 900 °C for 5 h before reducing the catalyst for the reaction. Baseline performance for unpromoted LaCuO₃ follows setup parameters detailed in earlier work [8].

2.2 Ethanol Dry Reforming Reaction

We tested reforming reactions in a stainless-steel tubular reactor in continuous mode, containing 100 mg of catalyst packed between quartz wool in the middle of the reactor. The reactor tube was heated by using a vertical furnace from 973 to 1073 K under atmospheric pressure. Prior to the EDR reaction, the calcined catalyst was reduced by flowing 50% H₂/N₂ at 70 mL/min and 973 K for 2 h. The EDR reaction was carried out at a stoichiometric ratio of feedstocks, ethanol: CO₂ = 1:1; partial pressures $P_{C_2H_5OH} = P_{CO_2} = 20$ kPa. Ethanol was injected into the reactor by using the calibrated syringe pump, while H₂, N₂ and CO₂ flows were fed by the Alicat mass flow controllers. The reactor outlet was connected to sample bags. We quantified product stream compositions online using gas chromatography (Agilent 6890 GC). We also studied catalyst deactivation to determine longevity. The conversion and yield were calculated by using the equations reported in our previous work [8] while the selectivity of products, *S*, was calculated as in Eq (3).

$$S_i = \frac{F_i}{\sum F_i} \quad (3)$$

where *F_i* represents the molar flow rate of species *i*. Mathematical fitting was conducted using SigmaPlot.

2.3 Catalyst Characterization

Crystalline phases of catalysts were analysed using a Rigaku MiniFlex II XRD (Cu Kα radiation, λ = 30 kV, 15 mA) scanned over 3° ≤ 2θ ≤ 80° at 1 °/min with 0.02° step size. Phase identification was completed via Match! software. Temperature-programmed reduction (TPR) was conducted on a PerkinElmer Pyris 1 thermogravimetric analysis (TGA) system using 20 mg of sample heated at 10 K/min from 373 K to 1023 K and held for 30 min under 20% H₂/N₂ (20 mL/min). Fourier transform infrared spectroscopy (FTIR) spectra (500–4000 cm⁻¹) were collected on a Nicolet iS5 spectrometer. Surface morphology and elemental compositions of spent catalysts were recorded using a scanning electron microscope with energy-dispersive X-ray spectroscopy (SEM-EDX), Hitachi TM3030 Plus system and TECNAI G2 20 Twin. Surface binding states were characterised by X-ray photoelectron spectroscopy (XPS) (JEOL JPS-9200, Al Kα source, 300 W, pass energy 10 eV calibrated to the C1s signal at 284.6 eV).

3. Results and Discussion

3.1 Catalytic Reforming Performance

We tested the catalytic impact of potassium promotion on  under stoichiometric feed conditions at 1023 K. Each run used a different fresh catalyst sample. Reactant conversion profiles as a function of potassium loading are illustrated in Figure 1(a). Initial substitution (25 wt%) increased reactant conversions compared to unpromoted LaCuO₃, elevating conversion by roughly 11% above the baseline 75% value reported in previous literature [11]. The conversions increased with the addition of K promotion. However, higher potassium loadings (*x* > 0.25) led to a progressive decline in conversion, fitting a Gaussian peak response (*R*² > 0.98) by the Gaussian peak model, Eq. (4)

$$X = A \exp \left[\frac{-(W_K - B)^2}{2W_K^2} \right] \quad (4)$$

This model was also used in Figure 1(b). This conversion suppression at elevated potassium levels stems from active site coverage by excess alkali domains and reduced surface area, which impedes reactant chemisorption. Nevertheless, the decrease occurred at 1023 K after 25% promotion of potassium, but when it was compared to the previous results in our report elsewhere [8], which was without potassium promotion, CO₂ conversion was 75%. The increase was about

11% due to 25% potassium promotion. This difference was also reflected in the product selectivity plots exhibited in Figure 1(b). The selectivity of carbon monoxide and methane declines with potassium promotion through the same model. Nonetheless, the model fit for methane selectivity is only about 90% R^2 due to fluctuations at 50 and 75 wt% potassium promotion. Hydrogen selectivity also dropped under the power model, but only slightly, indicating low sensitivity to potassium promotion. Similarly, carbon monoxide and methane yields dropped with potassium promotion in Figure 1(c), and the drops were greater than the hydrogen yield. We used exponential decay and rational-function models to fit carbon monoxide and methane yields, while a power equation fit the hydrogen yield, with $R^2 > 95\%$ for all. Figure 1(d) presents the changes of ratio based on carbon monoxide for hydrogen and methane against promotion of potassium. The H_2/CO ratio responded inversely to the CH_4/CO ratio. The H_2/CO ratio is higher than unity, suggesting hydrogen production through dehydrogenation of ethanol [12]. The graph showed a maximum H_2/CO ratio and a minimum CH_4/CO ratio at 50 and 75 wt% potassium promotion, respectively. When the H_2/CO ratio is compared with ethanol conversion, the trend is opposite, implying that the increase in the ratio did not track the drop in ethanol conversion. Nevertheless, the ratio remains within the typical syngas feedstock range for Fischer-Tropsch synthesis to produce long-chain hydrocarbons and green fuels [13]. The catalyst with the highest H_2/CO ratio, $La_{0.75}K_{0.25}CuO_3$, was selected to determine the effect of reaction temperature.

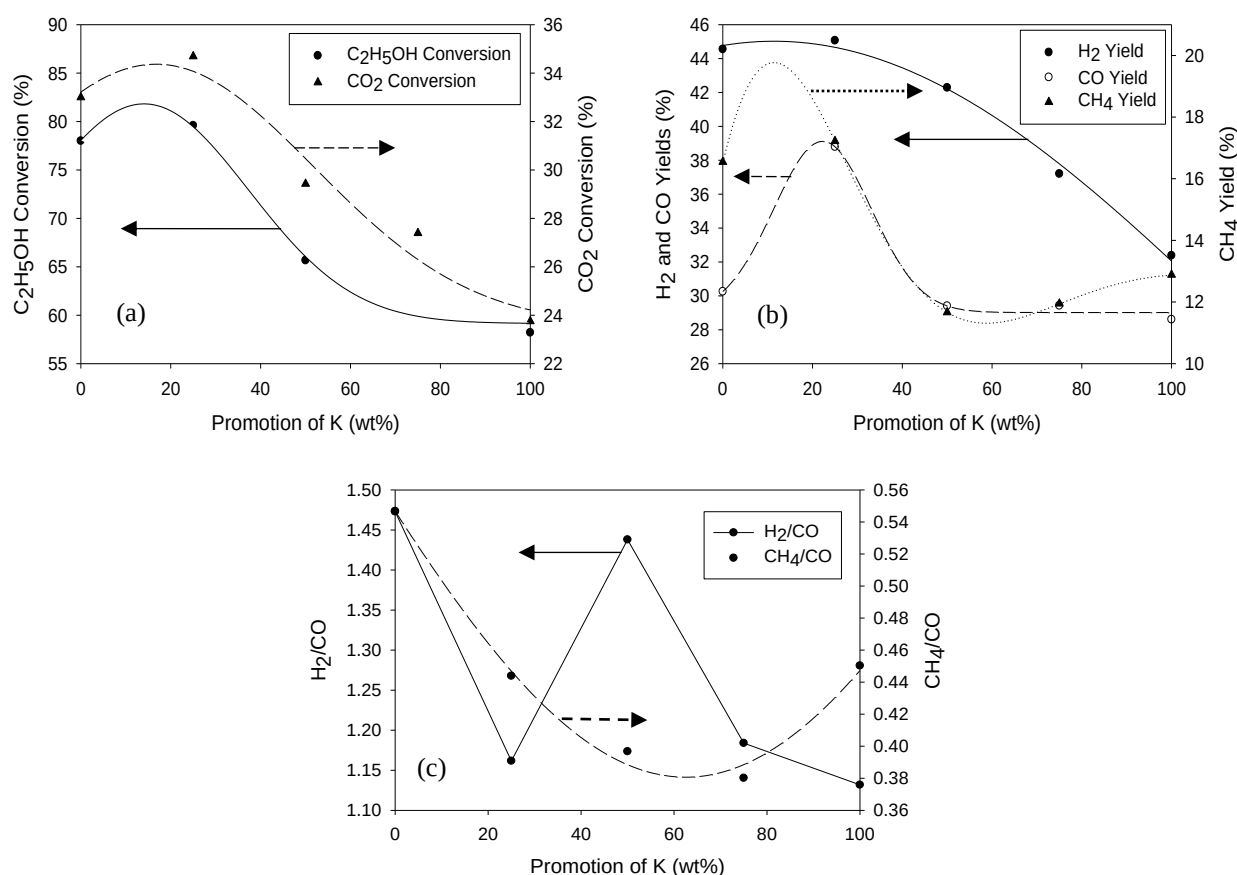


Figure 1. Analysis of (a) reactant conversions, (b) product yield and (c) product ratio for various levels of potassium promotion. Dots are experimental data, and trendlines plot calculated data from fitted models

Figure 2 shows the results of analyses on the EDR reaction at 4 different reaction temperatures using the $La_{0.75}K_{0.25}CuO_3$ catalyst. Each run used fresh catalyst samples. The concentrations of reacting materials were also determined by GC at steady state, when no change was recorded. Figure 2(a) displays the conversion of reactants as a function of reaction temperatures. Both conversions correlate linearly to the reaction temperatures at about the same gradient of 0.17, implying consistent reactions regardless of different heating. Nevertheless, ethanol conversion was initially 2.5 times higher than CO₂ conversion at 973 K. At 1073 K, it was 2 times higher, suggesting more CO₂ conversion at higher reaction temperatures. Ethanol conversion at a higher-than-stoichiometric ratio in the dry reforming reaction suggests ethanol decomposition, as reported by Wenju and Yaquan [14] in their thermodynamic analyses. Figure 2(b) clearly shows the decline in methane, another product from a different ethanol decomposition route as expressed in Eq. (4), and this decline follows a sigmoid model with reaction temperature.



H₂ and CO selectivity increased similarly in the same model as in Eq. (5);

$$S_i = \frac{a + bT}{1 + cT} \quad (5)$$

where $i = \text{H}_2$ and CO , a , b and c are the equation parameters, which means they will reach a maximum indicated by the parameter of a at infinite temperature. The maximum selectivity of H_2 and CO are 45.6 and 40.3 %, respectively, while the ratio of H_2/CO is between 1.5 and 1.6, which is suitable for the FT synthesis reaction. H_2 and CO yields increased with increasing reaction temperature. Figure 2(c) shows H_2 , CO and methane yields as a function of the reaction temperature. Running the EDR reaction at high temperatures would increase H_2 and CO yields but not methane. Both yields and the FT synthesis feedstocks increased with power, or sigmoidally, to a maximum at infinite temperature.

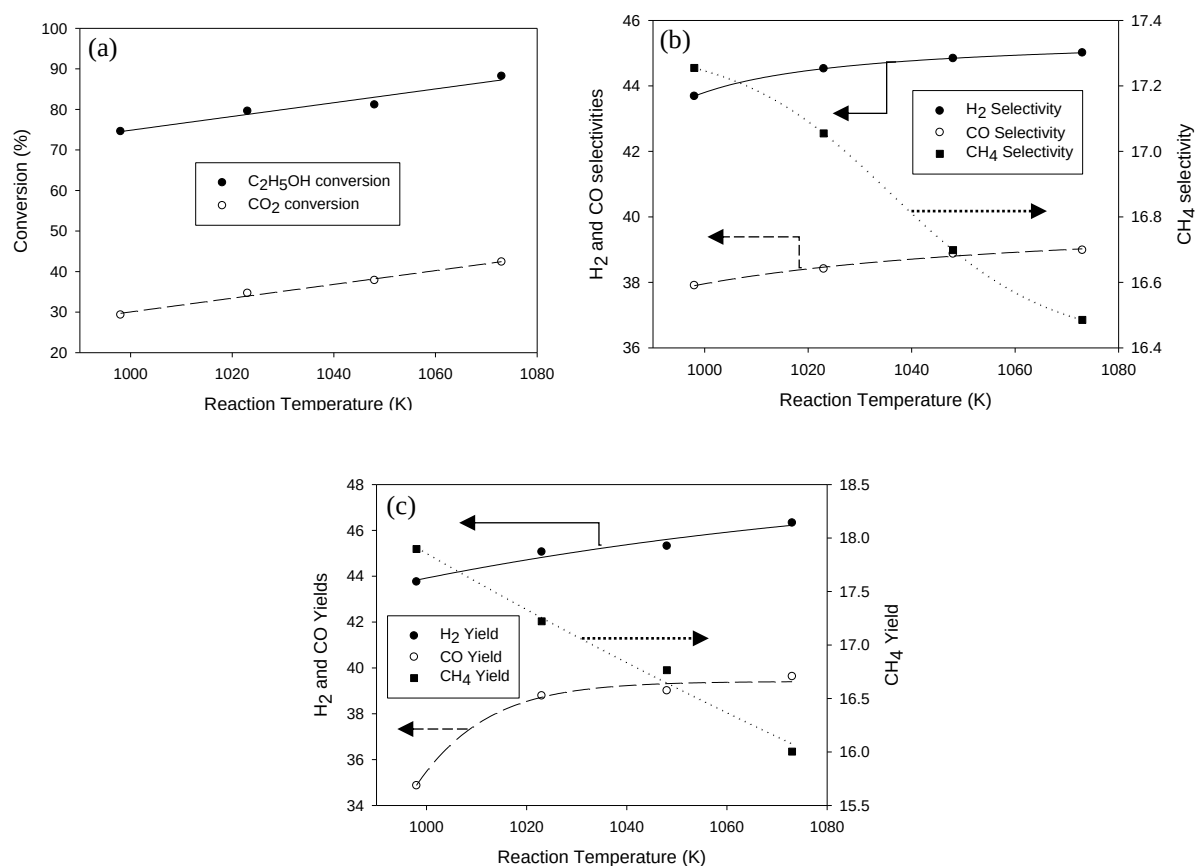


Figure 2. Analysis of (a) reactant conversions, (b) production selectivity and (c) product yield against EDR reaction temperatures for the $\text{La}_{0.75}\text{K}_{0.25}\text{CuO}_3$ catalyst. Dots are experimental data and trendlines plot calculated data from the fitted models

3.2 Characterisation of the Catalysts

3.2.1 Fourier transform infrared spectroscopy

The catalyst samples were analysed using FTIR spectroscopy, and the resulting spectra in the range of $500\text{--}4000\text{ cm}^{-1}$ were compared with the mineral spectra library in the data acquisition and analysis software and are presented in Figure 3. The region between 500 and 900 cm^{-1} contains absorption bands characteristic of metal-oxygen (M-O) bonds. Specifically, the transmittance dips at approximately 577 cm^{-1} (1), 666 cm^{-1} (2), and 808 cm^{-1} (3) correspond to the stretching vibrations of lanthanum-oxygen, potassium-oxygen, and copper-oxygen bonds, respectively. Furthermore, the bands observed at 1967 cm^{-1} (4), 2113 cm^{-1} (5), 2366 cm^{-1} (6), and 2506 cm^{-1} (7) are attributed to the stretching or combination modes of adsorbed hydroxyl ($-\text{OH}$) groups or atmospheric CO_2 interference, which is common in this region of FTIR spectra.

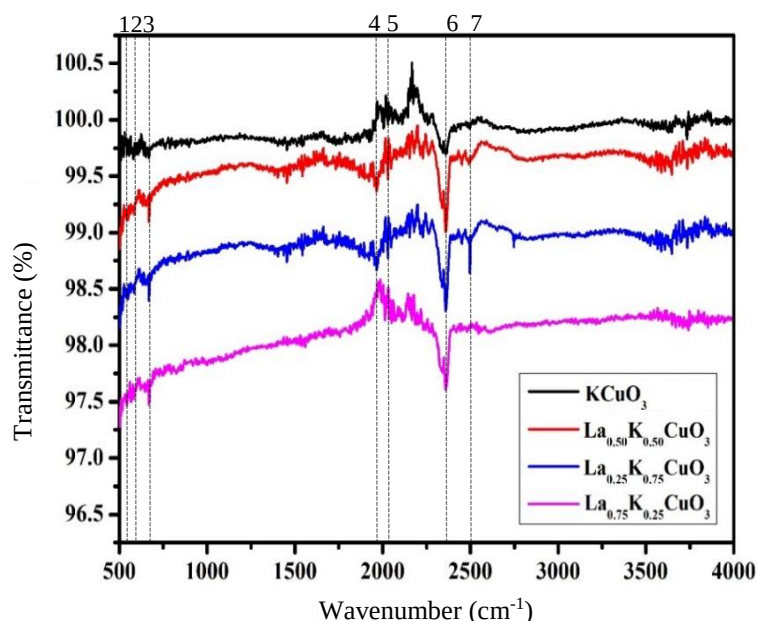


Figure 3. FTIR analysis of catalysts: (a) $\text{La}_{0.75}\text{K}_{0.25}\text{CuO}_3$, (b) $\text{La}_{0.50}\text{K}_{0.50}\text{CuO}_3$, (c) $\text{La}_{0.25}\text{K}_{0.75}\text{CuO}_3$ and (d) KCuO_3

3.2.2 Temperature-programmed reduction

The copper oxide component in a co-precipitated catalyst of CuZnAl oxides could have been first reduced at 200 °C [15]. Hence, in this study, as can be seen in Figure 4, complex copper-lanthanum oxide in the catalyst prepared along with potassium was probably reduced to metallic copper and lanthana at the first peak, as indicated by the TPR temperatures from 250 to 400 °C [16], which is also similar to the result of our work elsewhere [8] for copper-based perovskite. The promotion of potassium apparently produced at least 3 convoluted peaks in the copper oxide reduction in the TPR results, as illustrated in Figure 4(a), (c), and (d) within the same temperature range. The copper oxides might have undergone a stepwise reduction process: Cu^{3+} (usually appearing in perovskite) $\rightarrow \text{Cu}^{2+} \rightarrow \text{Cu}^0$, as also mentioned elsewhere [8]. However, these multiple peaks did not appear in the $\text{La}_{0.5}\text{K}_{0.5}\text{CuO}_3$ catalyst in Figure 4(b) where a single peak was formed at 323 °C. The uniform local environment around the copper atoms in the 50% K-doped sample creates a uniform electronic state. When the reduction temperature is reached (≈ 320 °C), the entire framework underwent a cooperative, rapid, and simultaneous reduction directly to metallic copper, merging the individual reduction steps into a single peak. This difference led to a peculiarity in the EDR result. Meanwhile, the peaks at TPR temperatures of 600 and 800 °C are the same and single for all samples, except for the one without lanthanum, where small peaks begin to rise in the plot at 600 °C. These peaks result from copper oxide reduction [17], and the XRD results indicate that LaCuO_3 was stable in the reducing atmosphere.

3.2.3 X-Ray diffraction

The peaks in the catalyst diffractograms were compared with the Joint Committee on Powder Diffraction Standards (JCPDS) database and revealed crystallinity, as shown in Figure 5. The single metallic phase of potassium was observed at 26.34°, while copper and lanthanum were at 43.49° & 50.50° and 15.43°, 30.50°, 54.78°, respectively. The average crystallite size of K and Cu estimated by Scherer equation are 6.74 and 9.3 nm, respectively. Lanfredi et al. [18] observed crystal sizes of CaTiO_3 that were doped using the ultrasonic spray-pyrolysis preparation method with potassium and copper close to 6 and 9 nm when the catalysts were calcined at 750 °C and 850 °C, respectively. Ogo et al. [19] reported that the addition of the potassium promoter to the catalyst caused the active phase to be surrounded by an amorphous potassium oxide. Thus, the crystalline structure of potassium with other metals resulted in combination rather than individual phases [18].

3.2.4 SEM-EDX

Figures 6 and 7 show SEM images of the spent catalysts at 10,000× Figure 6 magnification. EDX analyses were also carried out for the lanthanum-based perovskite with K promotion. All samples had carbon elements. Carbon was present without a clear structure in the $\text{La}_{0.75}\text{K}_{0.25}\text{CuO}_3$ catalyst at about 21 wt%, as shown in Figure 6(a). We observed filamentous carbon on the surface of the metal catalysts, confirming the results reported by Wang [20]. The $\text{La}_{0.50}\text{K}_{0.50}\text{CuO}_3$ and $\text{La}_{0.25}\text{K}_{0.75}\text{CuO}_3$ catalysts showed 12.27 and 33.67 wt% carbon, respectively, at the spots shown in their SEM images (Figure 6(b-c)). From previous works, the emergence of this carbon structure indicated a good tolerance catalyst towards carbon formation and reactant decomposition reactions [21, 22], but in this study, that is not the case,

as discussed in the reaction part before. Carbon weight composition differs, and carbon distribution varies from one spot to another within the same catalyst, with a variance of 2-5 wt%. This may be due to different activity across spots during the EDR reaction [23]. Spherical granules are visible in all images and are relatively clear in the KCuO_3 catalyst. This granule structure is likely a potassium oxide crystal, as reported in Figure 6(b-c), and Figure 7.

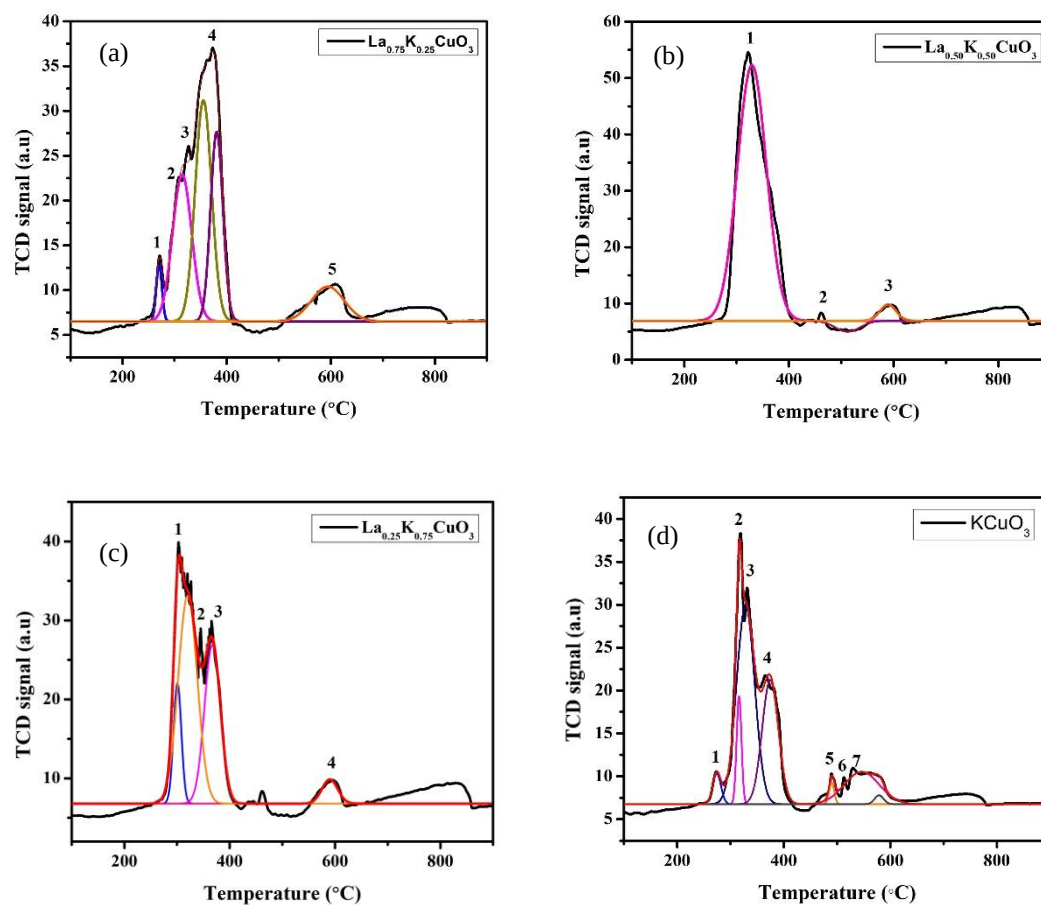


Figure 1. TPR analysis of (a) $\text{La}_{0.75}\text{K}_{0.25}\text{CuO}_3$, (b) $\text{La}_{0.50}\text{K}_{0.50}\text{CuO}_3$, (c) $\text{La}_{0.25}\text{K}_{0.75}\text{CuO}_3$, and (d) KCuO_3

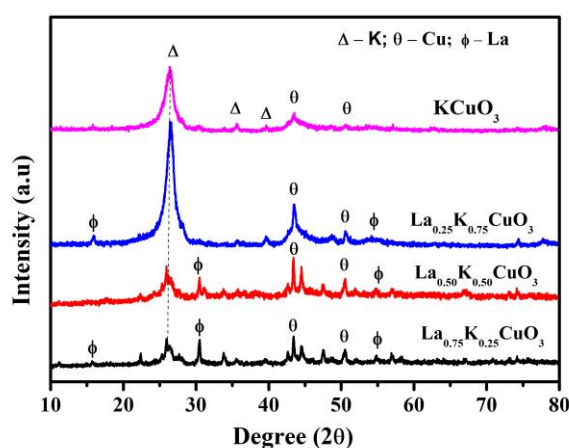


Figure 2. XRD analysis of $\text{La}_{0.75}\text{K}_{0.25}\text{CuO}_3$, $\text{La}_{0.50}\text{K}_{0.50}\text{CuO}_3$, $\text{La}_{0.25}\text{K}_{0.75}\text{CuO}_3$ and KCuO_3 catalysts

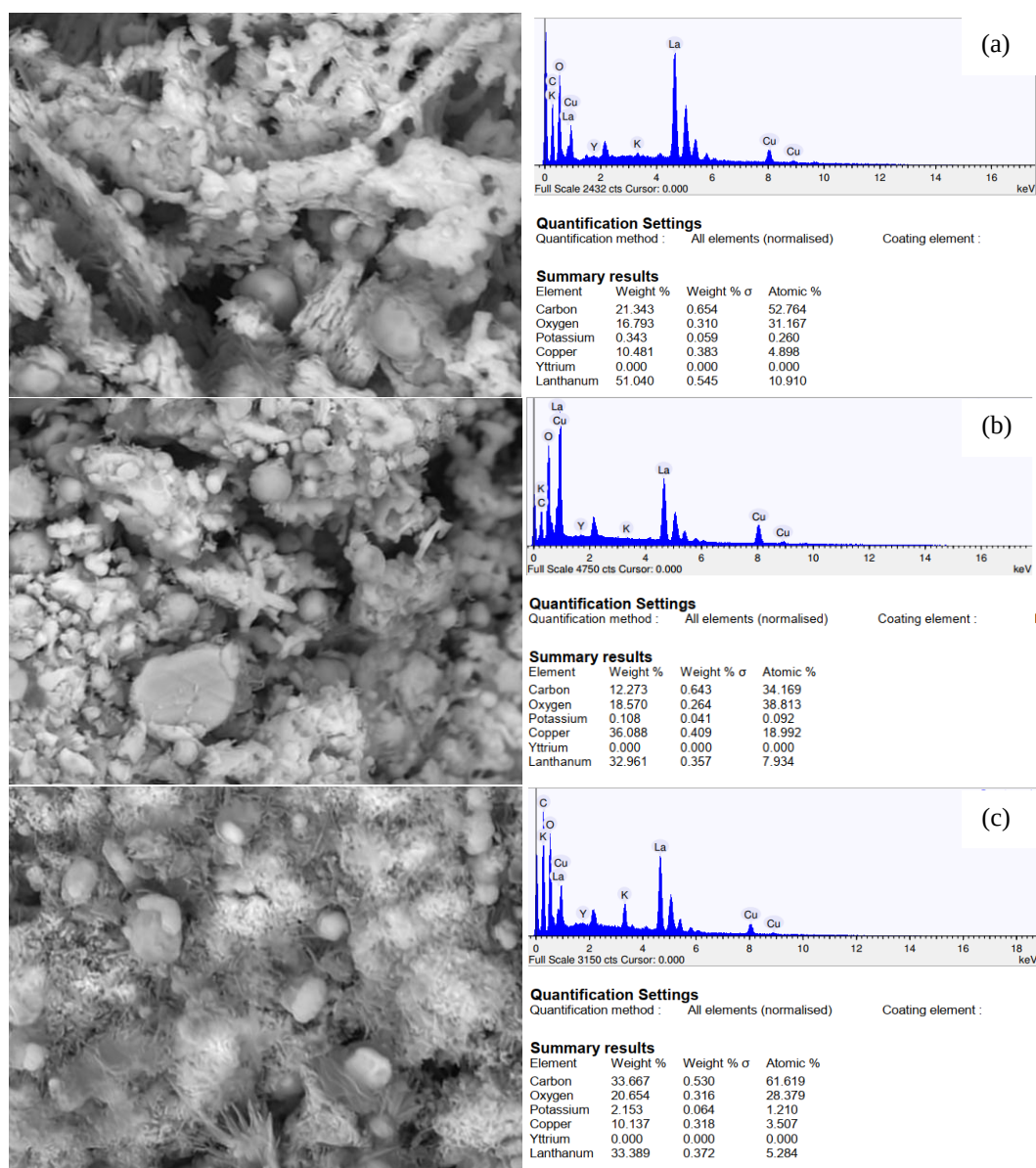


Figure 6. SEM-EDX analysis of spent catalysts: (a) $\text{La}_{0.75}\text{K}_{0.25}\text{CuO}_3$, (b) $\text{La}_{0.50}\text{K}_{0.50}\text{CuO}_3$ and (c) $\text{La}_{0.25}\text{K}_{0.75}\text{CuO}_3$

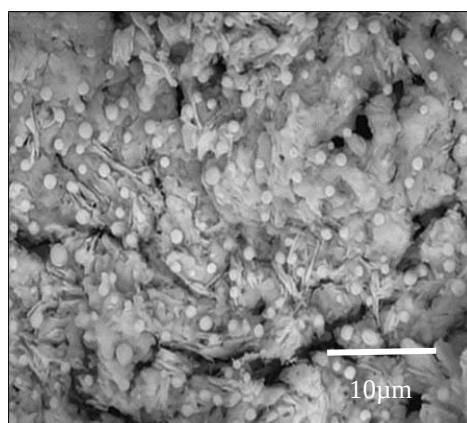


Figure 7. SEM analysis of spent KCuO_3 catalysts

3.2.5 X-Ray Photoemission spectroscopy

XPS analysis examined the surface valence state of potassium promoted onto lanthanum copper-based perovskite catalysts after the reaction. The binding energy of Cu 2p₃ and Cu 2p₁ in the $\text{La}_{0.75}\text{K}_{0.25}\text{CuO}_3$ catalyst was detected at 932.5 and 952.2 eV, respectively, in Figure 8(a), similar to the result of the $\text{LaNi}_{0.5}\text{Cu}_{0.5}\text{O}_3$ perovskite catalyst prepared and

reported by Ramesh et al. [24]. These copper valences are typical to CuO bonding rather than Cu₂O [25, 26]. Unfortunately, the latter was not present in the La_{0.25}K_{0.75}CuO₃ catalyst, probably because copper metal dominated. Figure 8(b) shows the same two copper electron valence states in both catalysts, La_{0.5}K_{0.5}CuO₃ and KCuO₃. Potassium oxide was detected at 292.2 and 294.7 eV in the KCuO₃ catalyst, as can be seen in Figure 8(c), which is different from the range of binding energy, which was between 527 and 535 eV when potassium oxide was prepared with silica [27]. This binding energy decreased as the potassium content decreased, as shown by the La_{0.5}K_{0.5}CuO₃ catalyst. Figure 8(d) displays the binding energies of 838.5 and 855.2 eV for La 3d₅ and La 3d₃, respectively, which are characteristic of lanthanum oxide [28].

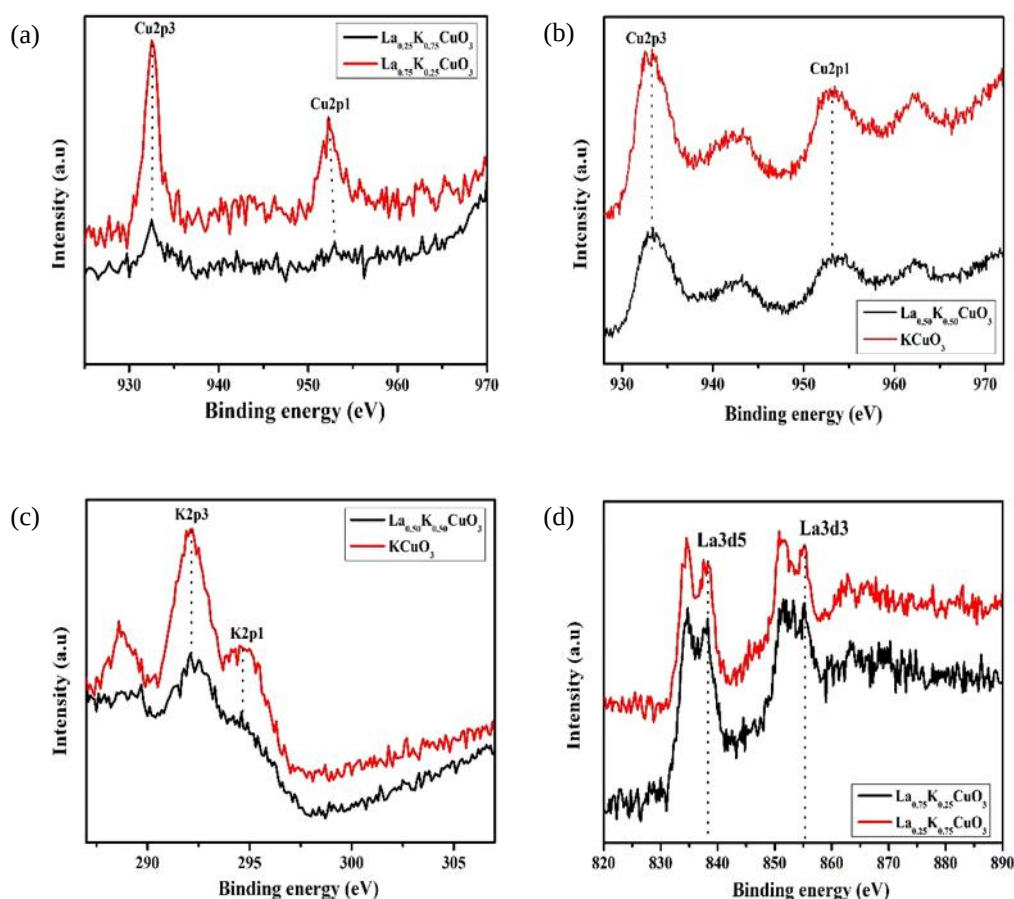


Figure 8. XPS analysis of catalyst for copper in (a) and (b), potassium in (c) and lanthanum in (d)

4. Conclusions

The catalysts of lanthanum copper-based perovskites promoted with potassium (La_{1-x}K_xCuO₃) were tested in a stainless-steel tubular reactor at various reactant partial pressures (20-50 kPa) and various reaction temperatures at 1073 K by using the EDR reaction at 1 atmospheric pressure. Adding potassium after 25 wt% decreased reactant conversion and product selectivity and yield. However, the hydrogen: carbon monoxide and methane: carbon monoxide ratios reach a maximum and a minimum at 50 wt% and 75 wt% potassium addition, respectively. Nevertheless, the first ratio as syngas is higher than unity for all potassium promotions. The ratio difference might be due to different TPR results shown by 50 wt% promotion of potassium and low carbon deposition in the SEM-EDX results on this catalyst. Filamentous carbon is also very clear than others in the micrograph of the catalyst.

Acknowledgements

The authors are thankful to all laboratory personnel of Faculty of Chemical and Process Engineering Technology, Universiti Malaysia Pahang Al-Sultan Abdullah.

Funding

This work was supported by Universiti Malaysia Pahang Al-Sultan Abdullah under the grants of fundamental research grant [RDU190377] and student research grant [PGRS180367].

Declaration of Competing Interests

The authors declare no conflicts of interest.

CRedit Author Contribution Statement

A. Ramkiran: Methodology; Analysis; Visualisation; Writing: original draft.

M. Sabri Mahmud: Methodology; Investigation; Funding Acquisition; Project Administration; Supervision; Writing: review & revise.

Availability of Data and Materials

Available on request: The datasets generated and/or analysed during the current study are available from the corresponding author on reasonable request.

Ethics Statement

This research does not require an ethics statement because it does not involve human participants, animals, or sensitive personal data.

Generative Artificial Intelligence Disclosure

AI-based tools were used solely for language editing and grammar refinement. No AI content generation or data interpretation was performed. All intellectual contributions are original and solely attributable to the authors.

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