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Original Research Article

Optimization of Synthesis Conditions and Characterization of a Ru-Promoted $CuO/ZnO/Al_2O_3$ Catalyst with Dual Applications

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ABSTRACT

Methanol is one of the most important industrial chemicals and is currently in high global demand. Industrial methanol production primarily relies on the hydrogenation of CO and CO_2, a process that simultaneously reduces carbon monoxide and carbon dioxide emissions while producing a valuable chemical product. In addition, the water-gas shift (WGS) reaction plays a crucial role in hydrogen production. Copper-based methanol synthesis catalysts are among the most advanced and widely used catalysts in the petrochemical industry. In industrial plants, synthesis gas is converted into methanol using these strategic catalysts. In the present study, copper, zinc, and aluminum nitrate salts were employed to investigate the feasibility of synthesizing a catalyst composed of copper oxide (CuO), zinc oxide (ZnO), and aluminum oxide (Al_2O_3). Furthermore, due to the requirement for effective adsorption and desorption of carbon monoxide, the effect of incorporating ruthenium into the catalyst formulation was also examined. The synthesized catalysts were characterized using X-ray diffraction (XRD), simultaneous thermal analysis (STA), and Brunauer-Emmett-Teller (BET) surface area measurements. The results indicate that the synthesis method used in this study is suitable for preparing this type of catalyst and that the resulting catalysts exhibit good thermal stability under operating conditions, particularly at temperatures around 260 °C.

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1. INTRODUCTION

Global warming is widely recognized by the scientific community as one of the most critical challenges facing life on Earth. The primary cause of this phenomenon is the increasing concentration of carbon dioxide (CO_2) in the atmosphere, largely resulting from the extensive consumption of fossil fuels (Atsonios et al.,2016), which has increased significantly in recent years (Saeidi et al.,2014). One promising strategy to mitigate this problem is the utilization of CO_2 as a feedstock for the synthesis of value-added chemicals (Aresta et al., 2013).

Methanol is a key platform chemical used as a precursor for the synthesis of a wide range of products. Up to 18 different chemicals can be derived from methanol, among which formaldehyde and acetic acid are the most important. In addition, methanol is used as an energy carrier and as a fuel in direct alcohol fuel cells. Consequently, global demand for methanol is expected to

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increase steadily (Dalena et al., 2018 & Bozzano et al., 2016).

Hydrocarbons are converted into other valuable chemicals, including hydrogen, through reforming processes in the presence of suitable catalysts. The water-gas shift (WGS) reaction, which is ubiquitous in reforming processes, plays a crucial role in controlling the concentrations of hydrogen and carbon monoxide. The WGS reaction is relevant to numerous industrial sectors, either directly or indirectly, including ammonia production in the fertilizer industry, oil refining, electricity generation in fuel cells, and transportation applications (Smith et al., 2010).

The ternary $CuO/ZnO/Al_2O_3$ catalyst is widely regarded as one of the most important catalysts for methanol synthesis from synthesis gas, as well as for hydrogen production from carbon monoxide via the WGS reaction.

Methanol is produced through the catalytic hydrogenation of carbon monoxide and carbon dioxide, with the composition of the feed gases varying significantly depending on the origin of the feedstock (Beck, Arik et al., 2024).

Early studies demonstrated that the binary copper-zinc oxide catalytic system exhibited promising activity (Lormand, 1925). The subsequent incorporation of additional oxides, most notably aluminum oxide, led to the development of industrially successful $Cu/ZnO/Al_2O_3$ (CZA) catalyst formulations (Wang et al., 2001). The activity and durability of CZA catalysts for methanol synthesis from $CO/CO_2/H_2$ feedstocks are significantly greater than the sum of those of their individual components, making this ternary system a classic example of catalytic synergism.

The CZA catalyst can be regarded as a ternary nanoparticle system composed of copper, zinc, and aluminum oxides. It demonstrates superior performance under industrial operating conditions while being produced from relatively inexpensive raw materials compared to noble-metal-based hydrogenation catalysts. Despite its long history of industrial application, the reaction mechanisms and the specific roles of each component in determining catalytic activity and stability remain subjects of extensive investigation and ongoing debate.

This efficient low-temperature methanol synthesis catalyst based on CuO, ZnO, and Al_2O_3, originally developed in the 1960s (Chinchen et al., 1988), remains the most widely used industrial catalyst to date (Zhong et al., 2020). Nevertheless, many aspects of the preparation, structure, and performance of copper-based catalysts continue to be actively studied (Dang et al., 2019).

Several factors influence the activity of synthesized catalysts (Kiener et al.,2003). For instance, increasing the co-precipitation temperature leads to an increase in particle size (Struis et al., 1996). A detailed investigation of the effects of pH and temperature on the properties of $CuO/ZnO/Al_2O_3$ ternary methanol catalysts has been conducted. In that study, the catalysts were prepared by the precipitation method using nitrate salts and sodium carbonate as precursors (Baltes et al., 2008, Behrens et al., 2011). The results showed that higher precipitation temperatures have a beneficial effect on catalyst performance. This improvement is attributed to a more uniform distribution of the components within the precipitate.

Catalyst promoters play a crucial role in achieving the key requirements of an effective catalyst, including high activity, improved selectivity, and long-term stability. In copper-based catalysts, copper crystallites serve as the primary active sites, and their catalytic performance has been strongly correlated with copper dispersion. The incorporation of promoters can increase the number of basic active sites available for methanol synthesis and enhance reaction rates. A variety of promoters have been investigated for copper-based methanol synthesis catalysts, including Au, ZrO_2, Pd, Th, Ce, Ru, Cs, Mg, and alkali metals (Saw et al., 2023). For example, Ru-promoted $Cu/ZnO/Al_2O_3$ catalysts have been reported to exhibit a significantly higher BET surface area (76.7 m^2/g) compared to catalysts promoted with elements such as Fe, Mg, Mn, Cr, Co, Zr, and Mo under similar preparation and reaction conditions (Safari et al., 2023). The use of a 2 wt% Ru/TiO_2 catalyst significantly improved CO conversion. In addition, the results showed a hydrogen recovery of 75%-96%, representing an approximately fivefold increase via the water-gas shift (WGS) reaction (Queiroz et al., 2018).

In the present study, a ternary catalyst composed of CuO, ZnO, and Al_2O_3 was synthesized via the co-precipitation method using nitrate salts as precursor materials. Catalyst stability and resistance to deactivation are critical factors for industrial applications. Therefore, considering the reactive nature of carbon monoxide and carbon dioxide, ruthenium particles derived from a ruthenium chloride precursor were incorporated into the catalyst. The resulting catalysts were systematically investigated and characterized to evaluate the effect of Ru addition on their structural and performance characteristics.

2. EXPERIMENTAL METHODS

2.1. SYNTHESIS OF CATALYST

Transition metal nitrate salts, including $Cu(NO_3)_2 \cdot 6H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, and $Al(NO_3)_3 \cdot 9H_2O$ (Royalex, India), along with sodium carbonate (Na_2CO_3; Royalex, India), were used as precursor materials for catalyst synthesis. Ruthenium chloride ($RuCl_3$; Merck) was employed as the precursor for ruthenium modification.

The synthesized $CuO/ZnO/Al_2O_3$ ternary catalysts and the Ru-modified ternary catalyst were designated

according to their composition and calcination temperatures, as summarized in Table 1. The abbreviations used throughout this study are also listed in the table.

Table 1. Characteristics of synthesized catalysts

No.	Catalyst composition	Sintering temperature (°C)	Catalyst name
1	CuO-ZnO-Al2O3	300	CZA-300
2	CuO-ZnO-Al2O3	350	CZA-350
3	CuO-ZnO-Al2O3	400	CZA-400
4	CuO-ZnO-Al2O3- Ru	350	CZAR-350

The co-precipitation method was employed for the synthesis of the ternary catalysts. Initially, 0.2 M aqueous solutions of copper, zinc, and aluminum nitrates were prepared using distilled water. In addition, a 0.3 M aqueous solution of sodium carbonate was prepared as the precipitating agent. Stoichiometric amounts of the nitrate solutions were transferred into a reaction vessel (a 500 or 1000 mL beaker) and thoroughly mixed. For the Ru-containing catalyst, the ruthenium precursor solution was added together with the nitrate solutions. Under these conditions, the initial pH of the solution was approximately 7.15.

The reaction vessel was placed on a magnetic stirrer, and the mixture was continuously stirred while the sodium carbonate solution was slowly added. During this stage, the pH of the solution increased to approximately 10.3, leading to the formation of a precipitate. After completion of the precipitation process, the suspension was stirred for an additional 3 h to ensure homogeneity. Previous studies have reported that higher pH values during co-precipitation (up to about 9.2) result in improved catalytic activity; this consideration was taken into account in the present work (Kipnis et al., 2022). Subsequently, the precipitated suspensions were allowed to age overnight at room temperature. The resulting precipitates were then washed several times with cold distilled water until a neutral pH was achieved. The washed samples were dried at 80 °C overnight.

The dried CZA precipitates were divided into three equal portions and calcined in a furnace at 300, 350, and 400 °C for 5 h. Based on the XRD and thermogravimetric analysis (TGA) results of the catalysts calcined at different temperatures, 350 °C was selected as the optimal calcination temperature for the synthesis of the Ru-modified catalyst. Accordingly, the CZAR sample was calcined at 350 °C for 5 h following the same procedure (Figure 1).

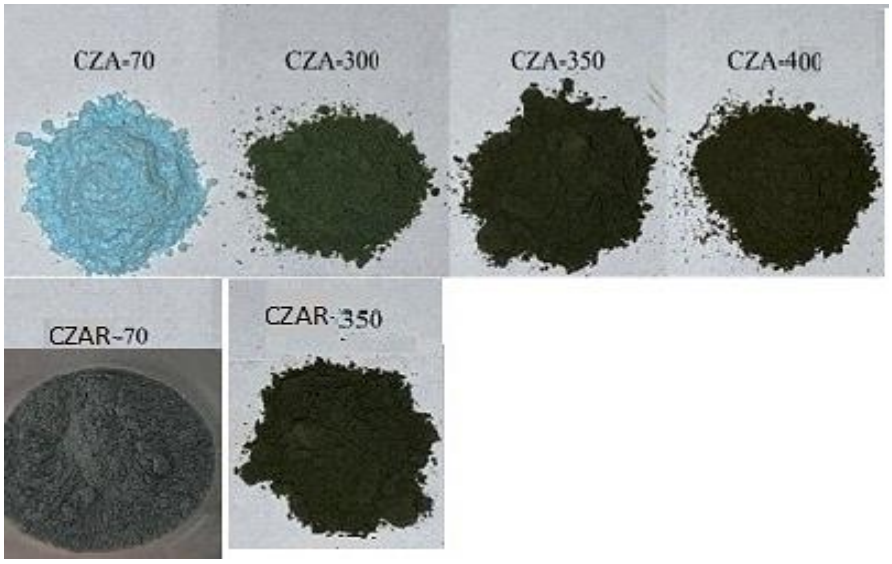


Figure 1. Synthesized CZA and CZAR catalyst powder at 70, and temperatures of 300, 350 and 400 °C

2.2. CHARACTERIZATION

Phase identification of the synthesized catalysts was carried out using X-ray diffraction (XRD) analysis with a Philips PW3710 diffractometer equipped with a Cu Kα radiation source (λ = 1.5406 Å). Diffraction patterns were recorded over a 2θ range of 10-80°. The thermal properties of the catalysts were investigated using thermogravimetric analysis (TGA). The measurements were performed with an STA 503 thermal analyzer (BAHR, Germany). The samples were heated under an argon atmosphere at a constant heating rate of 5 °C min^{-1} up to a final temperature of 600 °C.

The specific surface area and poro”Ity ’f the catalysts were determined using Brunauer-Emmett-Teller (BET) analysis. Nitrogen adsorption-desorption measurements were conducted using a Micromeritics Tristar II 3020 instrument (USA).

3. RESUTS AND DISCUSION

After synthesizing the catalysts using the method described in the previous section, the samples were characterized to identify their phases and structural properties.

The presence of a metal oxide with strong hydrogen adsorption on its surface is essential for the catalyst structure. In such systems, copper and the metal oxide must form a common active site, where carbon monoxide is adsorbed on copper while hydrogen is adsorbed on the metal oxide. Hydrogen spillover then occurs from the metal oxide, making activated hydrogen available for reaction with the adsorbed CO. In this study, ruthenium oxide was selected for this purpose. In methanol synthesis catalysts, zinc oxide acts as a basic component that neutralizes acidic sites in the alumina phase, thereby preventing the undesired conversion of methanol to dimethyl ether.

As mentioned earlier, one of the most common methods for identifying the crystalline phases present in catalysts is X-ray diffraction (XRD) analysis. Figure 2 shows the XRD patterns of the synthesized CZA samples.

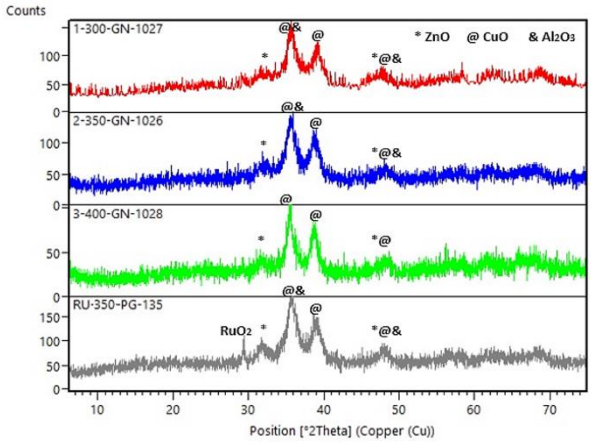


Figure 2. XRD spectrum of CZA catalysts synthesized at 300, 350, 400 and CZAR at 350°C

The XRD pattern of the CZA-300 sample, analyzed using Rietveld refinement, indicated the presence of 7% zinc oxide, 24% copper oxide, and 69% aluminum oxide. These phases correspond to the reference crystal lattice cards for hexagonal ZnO (010800074), monoclinic CuO (969015823), and rhombohedral Al_2O_3 (010760144), respectively. No impurity peaks were observed.

For the CZA-350 sample, the XRD results showed 13% zinc oxide, 29% copper oxide, and 58% aluminum oxide, consistent with the same reference lattice cards. No impurity peaks were detected. At this synthesis temperature, the copper oxide content increased, and considering its important role in methanol and hydrogen production reactions, 350 °C appears to be an appropriate temperature for catalyst synthesis.

The XRD pattern of the CZA sample synthesized at 400 °C revealed the presence of 6% zinc oxide and 94% copper oxide, while aluminum oxide was not detected. These phases matched the hexagonal ZnO and monoclinic CuO reference cards. The absence of detectable Al_2O_3 diffraction peaks in the CZA-400 sample should not be interpreted as the complete removal of aluminum from the catalyst. Rather, it is more likely that, after calcination at 400 °C, the alumina phase became highly dispersed, poorly crystalline, or amorphous, causing its diffraction peaks to fall below the detection limit of X-ray diffraction (XRD). Since XRD is sensitive only to crystalline phases, amorphous aluminum-containing species cannot be detected by this technique. Consequently, the XRD pattern remains dominated by the highly crystalline CuO and ZnO phases, and no significant changes are observed other than the disappearance of the Al_2O_3 reflections. The thermogravimetric analysis (TGA) results further support this interpretation, as the CZA-400 catalyst exhibited lower thermal stability, suggesting that the stable ternary CZA structure was partially disrupted during calcination rather than aluminum being chemically removed from

the catalyst. Given the known advantages of three-component catalysts in promoting the desired reactions, this temperature is not suitable for synthesizing a CZA catalyst.

Based on these results, 350 °C was selected as the optimal synthesis temperature for preparing the catalyst with the addition of ruthenium.

The XRD pattern of the ruthenium-containing catalyst showed 9% zinc oxide, 24% copper oxide, 62% aluminum oxide, and 6% ruthenium oxide. These phases correspond to the hexagonal ZnO (010800074), monoclinic CuO (969015823), rhombohedral Al_2O_3 (010760144), and orthorhombic RuO_2 (010880323) reference cards. No impurity peaks were observed. These findings demonstrate that the applied synthesis method successfully incorporated ruthenium oxide into the CZA catalyst, allowing its beneficial effects on methanol and hydrogen production to be utilized.

A summary of the XRD results for all synthesized catalysts is presented in Table 2.

Table 2. Characteristics from XRD results of the synthesized catalysts

catalyst	Al% rhombohedral	Zn% hexagonal	Cu% monoclinic
CZA-300	69	24	7
CZA-350	58	13	29
CZA-400	0	6	94
CZAR-350	62	9	24

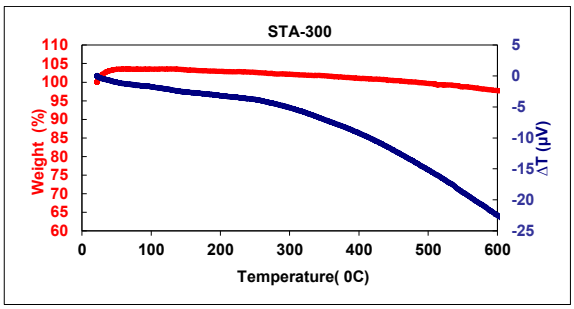
Since CZA catalysts operate in the temperature range of 200–300 °C for methanol and hydrogen production, thermal stability within this range is a critical parameter. Therefore, all four synthesized catalysts were evaluated by thermogravimetric analysis (TGA).

Figure 3 shows the weight changes of the catalysts from room temperature up to 600 °C.

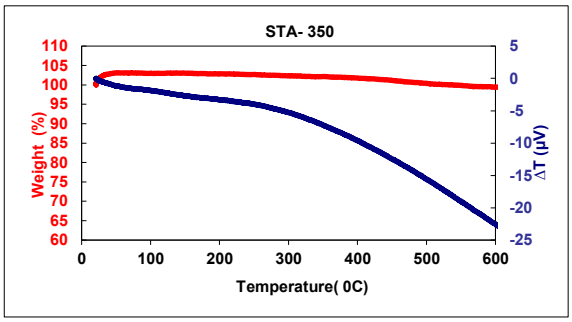
The CZA-300 sample exhibited no significant weight loss up to approximately 500 °C, followed by a gradual weight loss of about 5% between 500 and 600 °C. No abrupt weight loss associated with catalyst decomposition was observed, indicating good thermal stability in the operating temperature range (200–300 °C). Similarly, the catalyst synthesized at 350 °C showed negligible weight loss up to 600 °C, confirming its excellent thermal stability (Figure. 3(b)).

In contrast, the catalyst synthesized at 400 °C exhibited approximately 10% weight loss below 200 °C, additional weight loss between 200 and 300 °C, and a total weight loss of about 25% at 600 °C. Although no sharp decomposition step was observed, this catalyst showed inferior thermal stability compared to those synthesized at 300 and 350 °C. The absence of detectable aluminum oxide in the XRD analysis suggests that a stable CZA structure was not formed at this temperature, leading to reduced thermal stability (Figure. 3(c)).

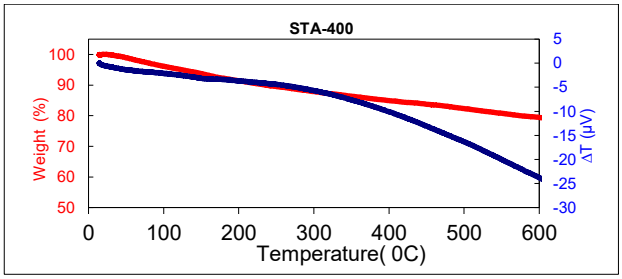
The CZAR catalyst showed no significant weight loss or signs of thermal degradation up to 600 °C. Therefore, this catalyst exhibits excellent thermal stability within the operating temperature range and is considered suitable for both methanol and hydrogen production (Figure. 3(d)).



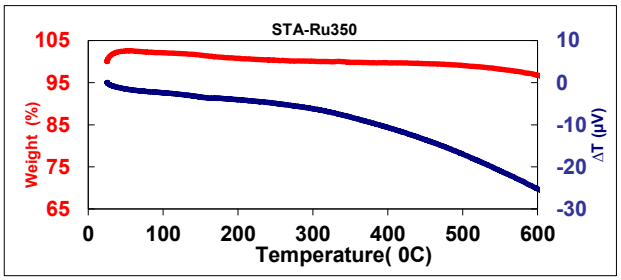
(a)



(b)



(c)



(d)

Figure 3. TGA results of synthesized catalyst (a) CZA at 300°C , (b) CZA at 350°C, (c) CZA at 400°C, (d) CZAR at 350°C

The CZAR catalyst showed no significant weight loss or signs of thermal degradation up to 600 °C. Therefore, this catalyst exhibits excellent thermal stability within the operating temperature range and is considered suitable for both methanol and hydrogen production (Figure. 3(d)).

Considering both structural integrity and thermal stability, 350 °C was identified as the optimal synthesis temperature. Consequently, the catalysts synthesized at this temperature, with and without ruthenium (CZA and CZAR), were subjected to BET surface area analysis.

Figures 4 and 5 present the nitrogen adsorption–desorption isotherms and pore size distributions of the CZA and CZAR catalysts, respectively. As shown in Figure 4, the isotherms exhibit type IV behavior with an H2-type hysteresis loop in the relative pressure range of 0.5–1.0, indicating the presence of mesoporous structures (Vafaee Zonouz et al., 2024). This behavior suggests a complex pore network in which pore connectivity and network effects play a significant role. Figure 5 confirms that the pore sizes of the samples fall within the micro- and mesoporous ranges. During calcination, the hydrotalcite precursor decomposes, and hydroxide and carbonate ions are removed, resulting in pore formation through the release of H_2O and CO_2. This process involves the collapse of larger pores and the generation of new, smaller pores. Notably, the CZAR catalyst exhibits the largest pore size, indicating a significant evolution of pore structure due to the presence of ruthenium.

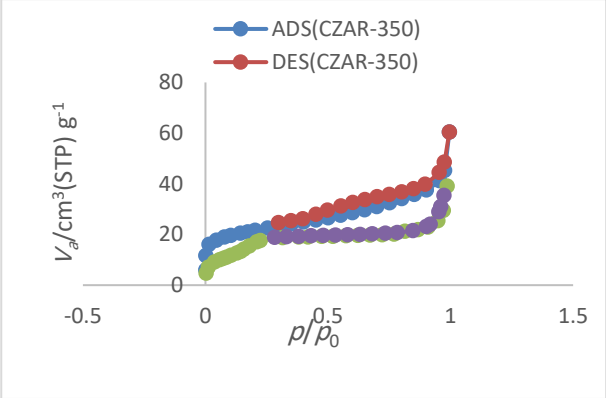


Figure 4. N2 adsorption- desorption of CZAR and CZA-350 catalysts

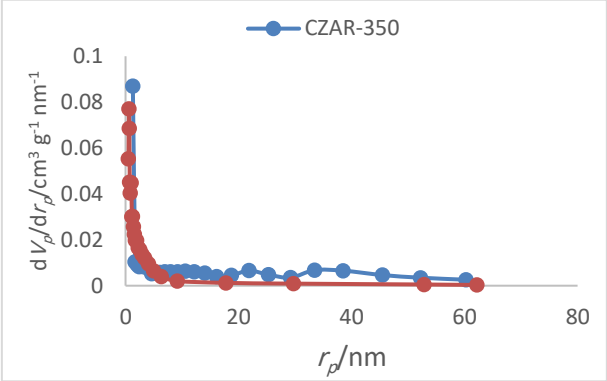


Figure 5. Pore size distribution of CZAR-350 and CZA-350 catalysts

The BET results show that the ruthenium-containing catalyst (CZAR) has a higher specific surface area than the ruthenium-free catalyst (CZA). This increased surface area is expected to enhance catalytic activity by improving reactant accessibility to active sites. An increased pore fraction facilitates mass transfer and improves reaction efficiency, thereby enhancing overall catalyst performance.

Table 3 summarizes the specific surface area, total pore volume, and average pore size of the catalysts synthesized at 350 °C (CZA and CZAR).

Table 3. BET analysis parameters of synthesized CZAR-350 and CZA-350 catalysts at 350 °C

Catalyst	BET area (m^2/g)	Total pore volume (cm^2/g)	Average pore diameter (nm)
CZA-350	76.81	0.2012	2.821
CZAR-350	89.23	0.574	2.706

4. CONCLUSION

In this study, a simple yet highly efficient synthesis strategy was employed to prepare a ternary catalyst composed of copper, zinc, and aluminum oxides using nitrate salts as precursors. Given the beneficial effect of noble metals on the performance of ternary catalysts, a ruthenium-containing catalyst was also synthesized. The key industrial relevance of the prepared catalysts lies in their dual functionality for methanol synthesis and hydrogen production via the water-gas shift reaction. The synthesized catalysts were systematically characterized using XRD, TGA, and BET analyses.

The results demonstrate that the proposed synthesis method is effective for producing both CZA and CZAR catalysts. Based on XRD phase analysis, 350 °C was identified as the optimal synthesis temperature. Thermogravimetric analysis revealed that all catalysts synthesized within this temperature range, except for the sample prepared at 400 °C, exhibit good thermal stability under operating conditions (200-300 °C). Furthermore,

BET analysis showed that the ruthenium-containing catalyst (CZAR) possesses a higher surface area and improved pore structure compared to the ruthenium-free catalyst (CZA). These structural advantages are expected to enhance catalytic performance in both methanol synthesis and hydrogen production.

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