

Investigation of the Synthesis and Reactor Evaluation of Alumina-Supported Cu Catalysts on CO Conversion in a WGS Reaction

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ABSTRACT: Heterogeneous CuO-ZnO/Al₂O₃ is widely used in various petrochemical plants to synthesize a low-temperature water gas shift reaction. Six different synthesis routes, co-precipitation, deposition-precipitation, ultrasonic deposition precipitation, incipient wetness impregnation, urea-co-precipitation gelation method, and combined incipient wetness impregnation-urea combustion, were compared for the synthesis of a catalyst with 20/5/75 weight ratios for CuO-ZnO/Al₂O₃. The products were analyzed and compared through XRD, SEM, BET analysis, and an activity test. The catalyst prepared by the incipient wetness impregnation-combustion urea method (IWI-Urea) showed the highest activity for CO conversion (47%) among the other synthesized products, with CO conversion ranging from 1.3 to 39%, and a commercial catalyst with 8.8% CO conversion. Additionally, the optimum operational condition for the activity test, including reaction temperature, space velocity, and steam-to-CO ratio, was studied on the catalyst with the highest activity (synthesized through the IWI-Urea method). Experimental results also indicated that at lower temperatures, a feed space velocity of 30000 h⁻¹ or higher led to the greatest CO conversions. Steam to CO ratio of 4 was also found to be optimum over the range of experimental conditions employed in this study. Reaction temperature was found to have the most significant effect on CO conversion compared with other operation factors employed in this study.

KEYWORDS: CuO-ZnO/Al₂O₃ catalyst; Catalyst preparation methods; Water-Gas Shift reaction; Conversion of carbon monoxide.

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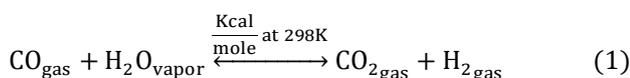
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INTRODUCTION

Hydrogen-powered fuel cells play an essential role in the creation of a clean energy system. Hydrogen produced conventionally by reforming reactions inevitably contains CO content which is harmful to polymer electrolyte membrane fuel cells (PEM-FC). Hence, the production of pure hydrogen to fuel PEM-FCs involves a series of processes such as hydrocarbon reforming, a water gas shift (WGS) reaction, preferential CO-oxidation, and/or methanation. Among these processes, WGS is the most crucial unit for H₂ purification and reducing the CO concentration in hydrogen fuel [1–4].

Synthesis gas (a mixture of hydrogen and carbon monoxide) is one of the primary feedstocks used in hydrogen production in chemical industries. Major industries that need to regulate the CO removal in the appropriate H₂/CO ratio to produce highly-pure hydrogen to be used as the feed of fuel cells, especially proton exchange membranes fuel cells (PEMFC) [5–7], are ammonium production plants[8–11] and hydrogen production plants[12, 13]. To regulate the H₂/CO ratio in industrial units, CO should be converted to CO₂ via the water-gas shift (WGS) reaction, as shown below:



The equilibrium CO conversion decreases with increasing the temperature because the reaction is exothermic [14, 15]. For this reason, WGS reaction is usually carried out in two stages. The first stage is carried out at high temperatures of about 350- 400 °C to bulk CO conversion and heat recovery, and the second stage is at low temperatures of about 180 to 220 °C to reach the equilibrium of the reaction and complete CO conversion. The standard commercial low-temperature shift (LTS) catalyst is comprised of CuO, ZnO, and Al₂O₃. This catalyst is activated by reducing CuO to metallic Cu, which is the catalyst's active site for the WGS reaction [16–18].

Cu-ZnO catalysts have been studied for use in the production of chemicals due to their high activity and relatively low price. Copper remains an excellent candidate for the active element in the new generation of WGS reaction catalysts and many other reactions [13, 19, 20]. Over the last decade, copper–ceria catalysts have been broadly studied for use in WGS reactions. Synthesis

research, microstructural investigations through multiple characterization methods, activity and stability tests, studies of the reaction mechanism, and detecting of the active sites have been conducted [6, 18, 20]. Copper catalysts have been prepared using many different methods, including the urea co-precipitation–gelation method [6,21], urea-nitrate combustion method [22,23], co-precipitation [25–32], impregnation [31], incipient-wetness impregnation [7], and deposition–precipitation (DP) [32–35]. *Sekizawa et al.* [36] studied the catalytic activity of Cu on alumina-mixed oxides support; they determined that Cu (30%)/Al₂O₃–ZnO had the highest activity in the water–gas shift reaction. Furthermore, *Utaka et al.*'s investigation[37] revealed that the activity of the catalyst depends on the crystallinity and surface area and that CO removal largely depends on gas velocity.

Different studies have concentrated on various aspects of the WGS reaction. In some cases, controversial and sometimes contradictory results have been reported. For example, one study [38] shows increasing the reaction temperature represent no improvement in CO conversion for any prepared catalysts in a high-temperature WGS reaction. Conversely, *Li et al.* [7] and *Tanaka et al.* [39] concluded that increasing the reaction temperature in certain cases results in the maximum conversion of CO for a low-temperature WGS reaction. However, they put less importance on the effect of other operational conditions on the WGS reactor performance. *Mahadevaiah et al.* [40] investigated the influence of the feed's steam to CO ratio (ranging from 2 to 8) on CO conversion. They found that greater CO conversion was obtained with steam to CO ratio of 6. *Bickford et al.* [33] studied the effect of space velocity on the WGS reaction operation and concluded that this parameter had no considerable impact on the catalyst activity. They claimed that the catalyst activity decreased slightly at very high space velocities. On the other hand, *Jeong et al.* [41] concluded that the CuOCeO₂ catalyst was one of the best catalyst candidates for low-temperature WGS reactions at very high gas hourly space velocity (GHSV). *Yahiro et al.* [42] found that catalyst activity increased by increasing the reduction temperature of the catalyst.

Water-gas shift reaction is reversible and exothermic; therefore, this reaction will be closer to equilibrium at lower temperatures. This research investigates different methods of catalyst synthesis and different operating

conditions to achieve the best performance for CuO/ZnO/Al₂O₃ catalyst at low temperatures. Firstly, catalysts prepared through various synthesis routes reported in the literature and the novel method proposed here (a combination of *incipient wetness impregnation* and *urea combustion method*) were compared in terms of their structural properties and catalytic performance. Secondly, the influence of operational conditions, including reaction temperature, space velocity, and steam to CO ratio, on the WGS reaction was studied.

EXPERIMENTAL SECTION

Materials

All chemicals and solvents were reagent grade. Water was distilled and deionized. Cu(NO₃)₂·3H₂O, Zn(NO₃)₂·6H₂O, Al(NO₃)₃·9H₂O, CO(NH₂)₂, and Na₂CO₃ were purchased from the Loba Chemie company. The γ -Al₂O₃ support was prepared by a co-precipitation method using Na₂CO₃ aqueous solution as precipitant at a temperature of 70°C, as proposed by *Zaherian et al.* [43].

Methods

Catalysts samples were prepared using the six methods described below:

• Co-precipitation (CP) method

The CuO-ZnO/Al₂O₃ catalysts were prepared with a co-precipitation method [24], [25]. Two aqueous solutions, one containing the desired amounts of M(NO₃)₂ (M = Cu, Zn) and Al(NO₃)₃·9H₂O (total cation concentration of 0.5M and CuO: ZnO: Al₂O₃ = 20: 5: 75 in weight percentage) as precursors and the other containing Na₂CO₃ (1M) as the precipitant, were added simultaneously under vigorous stirring at 70°C. pH was maintained at around 7 by regulating the flow rates of the Na₂CO₃ solution via a controller. The obtained precipitate was aged under stirring for one h at 70°C. After filtration, the precipitate was washed with distilled water, dried at room temperature for 48 h, and calcined in air at 450°C for four h.

• Deposition-precipitation (DP) method

The deposition-precipitation (DP) method used for catalyst preparation is described in the literature [32]. Synthesized Al₂O₃ was placed in a beaker and submerged in H₂O. Appropriate solutions of Cu(NO₃)₂·3H₂O and Zn(NO₃)₂·6H₂O in water were prepared. The salt solution

was added drop-wise to the Al₂O₃/ H₂O slurry. Cu(NO₃)₂·3H₂O and Zn(NO₃)₂·6H₂O aqueous solutions were added first, followed by a Na₂CO₃ aqueous solution under vigorous stirring at 70°C. The pH value was maintained at around 7. The obtained precipitate was aged under stirring in the mother liquor at 70°C for one h. After filtration, the precipitate was washed with distilled water, dried at room temperature for 48 h, and calcined in air at 450°C for 4 h.

• Ultrasonic deposition-precipitation (DP-Ultra) method

The entire process was similar to the DP method, except that during the aging time the slurry is stirred using a Misonix ultrasonic liquid processor at a power of 25W.

• Incipient Wet Impregnation (IWI) method

In this method a minimum amount of solvent should be added to the support in the incipient wet impregnation (IWI) method[33]. The catalyst support saturation limit (incipient wetness volume) was first determined by adding solvent drop-wise. The metal salts Cu(NO₃)₂·3H₂O and Zn(NO₃)₂·6H₂O were dissolved separately in a minimal amount of deionized H₂O. The salt solutions were added to the support powder dropwise. Next, a small amount of an appropriate solvent was used to wash out the support and remove the remaining salt. The impregnated supports were then oven-dried at 90°C for 24 h. After the drying step the catalysts were calcined at 450°C for four h.

• Urea-co-precipitation gelation method (CP-urea) method

The urea-co-precipitation gelation (urea-CP) method for support preparation is similar to that used by *Kundakovic et al.* [44]. An appropriate molar amount of salts Cu(NO₃)₂·3H₂O and Zn(NO₃)₂·6H₂O dissolved in 300 mL of deionized H₂O were placed in a beaker. Urea was dissolved in deionized water and added to the metal nitrate solution. The solution was heated at 90°C until it boiled and precipitation occurred. At the start of precipitation, the suspension was boiled for 2h to remove ammonia and age the support. The support was filtered and dried in an oven for 24h and then calcined at 450°C for 4h.

• Combination of urea-nitrate combustion and incipient wet impregnation method (IWI-Urea)

Here the catalyst was produced through a combination of the incipient wet impregnation method and the urea-nitrate

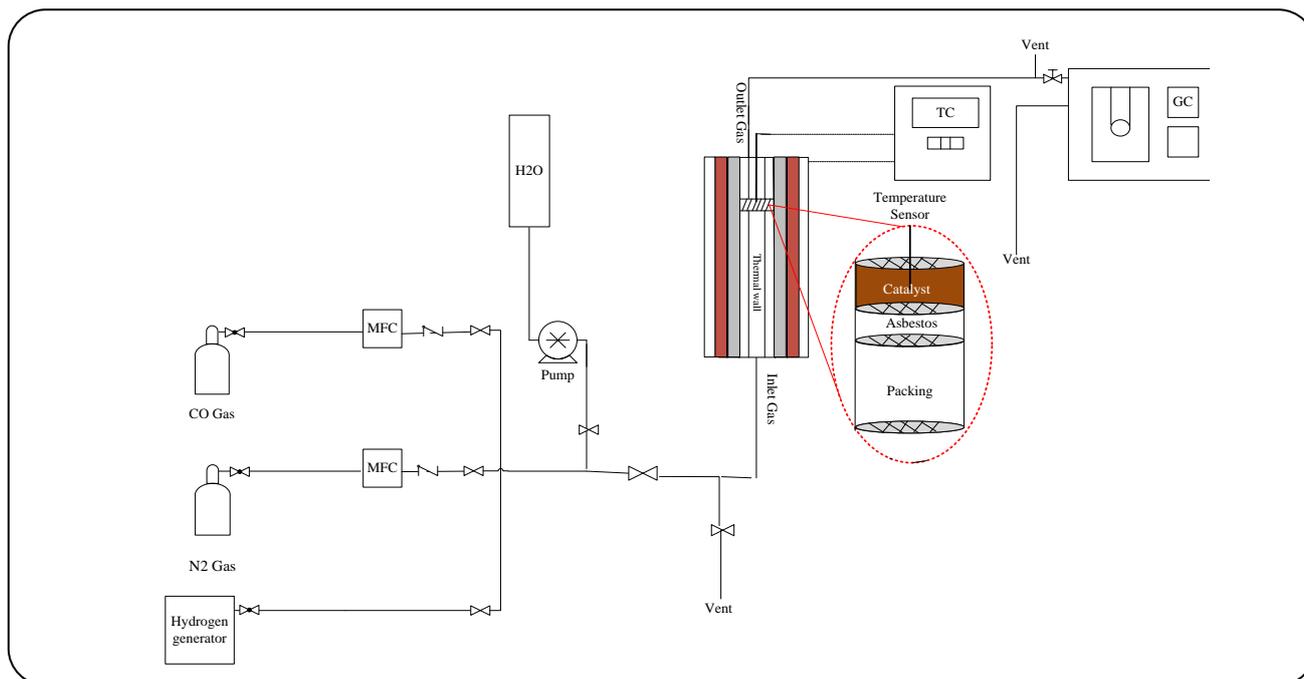


Fig. 1: A schematic of the reactor system.

combustion method. Solutions of metal salts $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and urea were added to the support powder dropwise to form a gel at a high temperature. This gel was heated until it released a brown gas and became utterly dark. The gel was subsequently dried in an oven for 24h and calcined at 450°C for four h.

Characterization instruments

Calcined samples were characterized via Scanning Electron Microscopy (SEM) and X-Ray Diffraction (XRD). XRD data were collected on a PHILIPS PW1800 diffractometer using $\text{CuK}\alpha$ radiation. Samples microstructures was observed by SEM-VEGA//TESCAN 30kv. The specific surface area and pore volume of each calcined sample were calculated via the BET method from the N_2 adsorption isotherms, which were acquired using a Micro metrics TriStar apparatus.

Activity test setup

A schematic of the reactor system used here is illustrated in Fig. 1. The system's major components consist of equipment for controlling the feed flow into the reactor, the reactor and its accessories (including a furnace and temperature control system), and an online gas chromatograph to analyze product gases. The flows of high purity CO, hydrogen, and nitrogen were controlled

by mass flow controllers and directed to the bottom of the reactor. Water was also injected into the bottom of the reactor through a pump. After being combined and heated, the incoming gases and steam passed through the catalyst bed where the WGS reaction would occur. The reactor inlet gases included CO, nitrogen, and steam. The outlet gases included CO_2 and hydrogen. A Philips PU4815 gas chromatography analyzed effluent gases after the outlet steam was condensed in a water trap to prevent damage to the gas chromatograph column. The gas chromatograph was calibrated before the experiment using a standard calibration gas sample obtained from Tarkib Alvand Incorporation.

Catalytic performance in WGS reaction

For all six prepared catalysts and a commercial catalyst, 1 gram of catalyst was passed through 35-60 mesh size and loaded into the reactor. Catalyst activity tests were conducted at 180°C using a feed consisting of 150 mL/min flow of N_2 , 30 mL/min flow of CO, and 120 mL/min flow of H_2O at atmospheric pressure. The outlet gases were injected into the GC in 15-minute time intervals for 2 hours during the stable state of the system (an hour after the beginning of the reaction).

The performance of the catalyst was evaluated in terms of CO conversion and H_2 selectivity defined as follows:

$$\text{CO Conversion} = \frac{(F_{\text{CO,in}} - F_{\text{CO,out}})}{F_{\text{CO,in}}} \quad (2)$$

$$\text{H}_2 \text{ Selectivity} = \frac{F_{\text{H}_2}}{(F_{\text{CO,in}} - F_{\text{CO,out}})} \quad (3)$$

Where $F_{\text{CO,in}}$ and $F_{\text{CO,out}}$ represent the molar flow of the CO at the inlet and outlet of the reactor, respectively. F_{H_2} is the hydrogen molar flow. In the following the sample with highest activity was selected to investigate the impact of three operational factors; reaction temperature, steam to CO ratio in the feed, and the space velocity on the catalyst activity.

RSM experiment design

For each experiment, 1 gram of catalyst was passed through 35-60 mesh size and loaded into the reactor. The reactor was then heated to 250°C and purged under nitrogen flow. Next, the catalyst was reduced in-situ at atmospheric pressure and 250°C for 3h before running a 1:1 mixture of H_2 and N_2 at a 60 mL/min flow rate. The reactor was then cooled to 150°C under nitrogen flow. Finally, the reactor was then heated to the desired reaction temperature with the feed flow rate and composition as specified by the Response Surface Methodology (RSM). Experiments were conducted for reaction temperatures in the range of 150 to 250°C, space velocities in the range of 25000 to 35000 $1/h$, and feed steam to CO ratios in the range of 4 to 8.

RESULTS AND DISCUSSION

Catalyst Characterization

Fig. 2 demonstrates the XRD patterns of the prepared catalysts. The peaks of the crystallite phase of CuO are recognizable at $2\theta=35.5^\circ$, 38.7° , and 48.7° . These peak's intensities are the largest in the sample prepared by the combined method (IWI-Urea) compared with the other samples. This may be due to the relatively lower loading (~5 wt. %) of ZnO phase and its homogeneous dispersion on the catalyst's surface. There were no peaks observed for ZnO.

Since a significant proportion of the prepared catalysts consisted of $\gamma\text{-Al}_2\text{O}_3$ support and the spectra of this material have a broad and diffuse peak, the fluctuations observed in the XRD spectra belong to CuO peaks.

The crystallite sizes for CuO phase is calculated by the Debye-Scherrer equation [45] based on the most intense peak and is listed in Table 1.

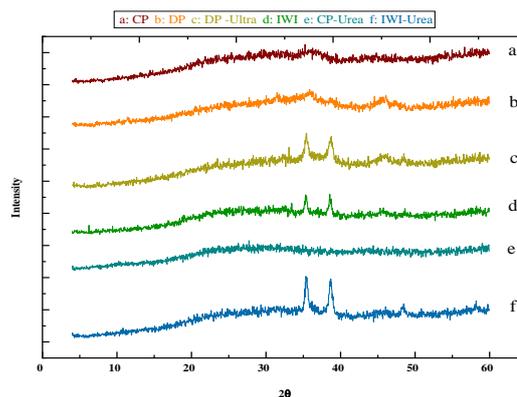


Fig. 2: XRD spectra of catalyst samples CP (a), DP (b), DP-Ultra (c), IWI (d), CP-Urea (e), IWI-Urea (f).

$$D = \frac{0.9\lambda}{\beta \cos \phi} \quad (4)$$

In equation (4), λ is the wavelength of X-ray Cu $K\alpha$, ϕ is the Bragg angle, and β is the full width at half maximum height. Since the peaks for the samples prepared by the CP and CP-Urea method were unrecognizable, their crystallite size cannot be calculated. This confirms the amorphous texture of these samples. Spectra of the other catalysts have narrow and intense peaks in the CuO phase, which is an evidence of the nano-sized formation of this phase in these samples. Comparing the XRD spectra of the prepared samples, the peaks for the CuO crystallite phase in the IWI-Urea sample had the highest intensity. In other samples, CuO peaks are not as intense showing that the metal oxide is finely dispersed.

Furthermore, BET results reveal that the co-precipitation method led to the lowest specific surface area of around 100 m^2/g for the CP and CP-Urea samples, see Table 1. The deposition-precipitation method and the incipient wetness impregnation method resulted the catalysts with the highest specific surface area and pore volume, ranging from 160 to 177 m^2/g and the pore volume ranging from 0.5 to 0.6 cm^3/g . However, these values for the catalyst prepared with the IWI-urea combustion method were medium with 120.9 m^2/g for specific surface area and 0.38 cm^3/g for pore volume.

Fig. 3 shows the SEM pictures of the prepared catalysts. The range of particle sizes and their frequencies were obtained using Microstructure Measurement software are presented in Fig. 4. The average particle size for each sample is reported in Table 2. As seen in Fig. 3,

Table 1: CuO crystallite size and BET results of the CuO-ZnO/Al₂O₃ catalysts prepared by CP, DP, DP-Ultra, IWI, CP-Urea and IWI-Urea methods.

Catalyst code	CuO crystallite size (nm)	BET (m ² /g)	Pore volume (cm ³ /g)
CP	-	103.08	0.109
DP	29.04	177.20	0.636
DP-Ultra	20.56	165.49	0.534
IWI	29.99	160.42	0.510
CP-Urea	-	99.81	0.107
IWI-Urea	69.43	120.92	0.386

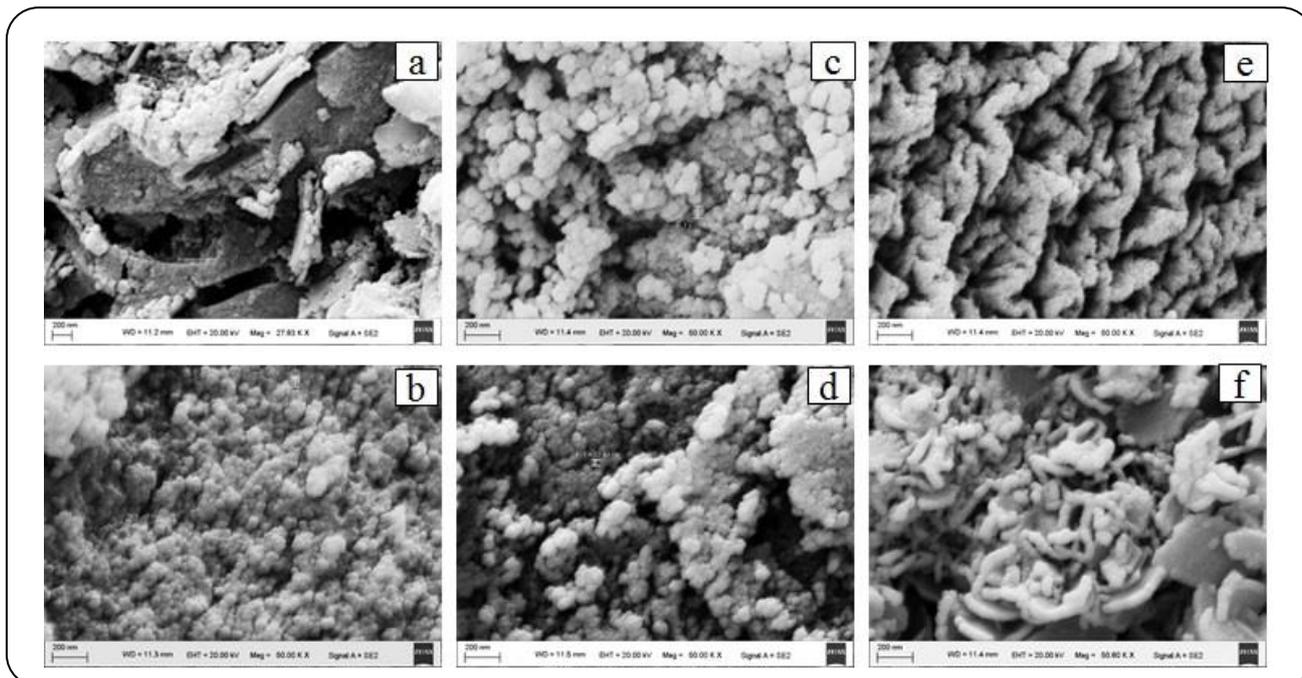


Fig. 3: SEM pictures of CuO-ZnO/ Al₂O₃ catalysts prepared by different methods: CP (a), DP (b), DP-Ultra (c), IWI(d), CP-Urea(e), IWI-Urea(f).

the sample prepared with the IWI-Urea method is proven to have the highest homogeneity in particles size. In this sample, the range of the particle size was between 60 and 110 nanometers, with most falling between 70 and 80 nanometers. According to Fig. 4, approximately 73% of particles have sizes smaller than 90 nanometers, indicating the nano-sized microstructure of the catalyst. SEM pictures confirmed the results obtained by the XRD spectra and revealed that the two samples prepared by the CP and CP-Urea methods have amorphous structures. The other samples tend to mostly have nano-sized particles with a rather fine size distribution.

In DP, DP-Urea, and IWI methods, the sizes of recognizable particles in the SEM pictures are extremely small. Although this characteristic is helpful in providing

a higher surface for the reaction in these samples, it arouses concern because these catalysts will face problem in a wet environment because of the competitive adsorption of water and CO; thus, their activity would decrease. Regarding the results of the SEM analysis, sample particles prepared by the IWI-Urea method have better homogeneity than the other samples.

Catalytic Performance in WGS Reaction

Catalyst activity tests were conducted at 180°C using a feed consisting of 150 mL/min flow of N₂, 30 mL/min flow of CO, and 120 mL/min flow of H₂O at atmospheric pressure. The outlet gases were injected into the GC in 15-minute intervals for 2 hours during the stable state of the system (an hour after the beginning of the reaction).

Table 2. Average particles size of the CuO-ZnO/Al₂O₃ catalysts prepared by DP, DP-Ultra, IWI, and IWI-Urea methods obtained from SEM pictures.

Catalyst code	average particle size (nm)
DP	46.79
DP-Ultra	54.26
IWI	50.31
IWI-Urea	81.04

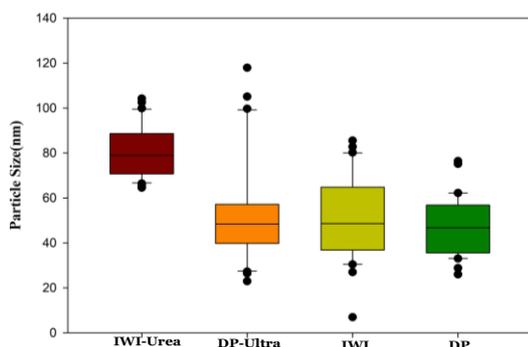


Fig. 4. The distribution of particle size was obtained from SEM pictures of the CuO-ZnO/Al₂O₃ catalysts prepared by DP, DP-Ultra, IWI, and IWI-Urea methods.

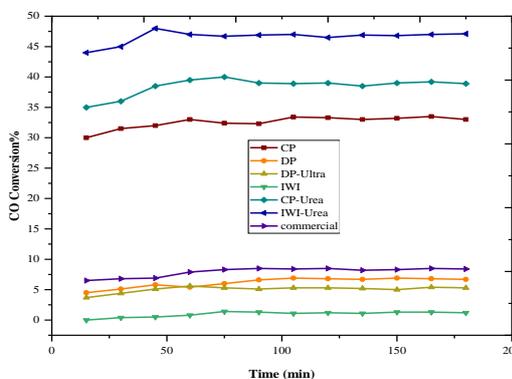


Fig. 5. CO conversion versus time from the start of the run for the CuO-ZnO/Al₂O₃ catalysts prepared by CP, DP, DP-Ultra, IWI, CP-Urea, and IWI-Urea method and commercial catalyst at 180°C with a feed flow rate of 150, 30, and 120 mL/min of N₂, CO, and H₂O, respectively.

CO conversion and H₂ selectivity are presented in Table 3 and Fig. 5 for all the six prepared catalysts and a commercial catalyst for comparison. As it can be seen

in Table 3, H₂ selectivity for all samples was acceptable and did not vary considerably from one sample to another. In terms of CO conversion, however, the activity of the catalysts synthesized by DP, DP-Ultra, and IWI methods was lower than that of the industrial catalyst. On the other hand, the catalyst prepared by IWI-Urea method proved to have the highest activity compared with other catalysts. So, the best catalytic performance was observed for the catalyst with optimal particle size in the range of 70-80 nm with the highest homogeneity in particle size.

Moreover, this catalyst also demonstrated higher activity than the industrial catalyst.

Optimum Operation Condition

Three factors considered in RSM experimental design were reaction temperature, steam to CO ratio in the feed, and space velocity (Table 4). The range of values for these parameters is chosen based on the previous studies [46], [47], [32], [16]. The three parameters considered here have been studied separately in terms of their effect on WGS reaction, while in the present study it is tried to elucidate their impact simultaneously when all of them vary.

The RSM analysis of experimental data resulted in an R² factor of approximately 85%. Table 5 shows the analysis of variance of the model obtained from the design of the experiment and the influence of factors on CO conversion. The significance or non-significance of the presence of each parameter in the model and their significance level can be interpreted using this table. As it can be seen, the P value for the factors of temperature and space velocity is below 0.05, which shows the significance of these parameters on CO conversion. The effect of each factor illustrated as a percentage in the pie chart of Fig. 6 indicates that reaction temperature has the most significant effect on CO conversion, followed by space velocity, while steam to CO ratio has the least effect on CO conversion amongst the three factors considered.

Space velocity demonstrated different behaviors with distinct optimal values at each temperature. Fig. 7a shows the simultaneous effect of temperature and space velocity on CO conversion. As it can be seen, at lower temperatures, the space velocity of feed ~30000 1/h is optimum, while at higher temperatures, the optimal value is 35000 1/h.

The reaction temperature was the most important factor influencing CO conversion. The WGS reaction is reversible and exothermic. This is usually carried out in two stages.

Table 3: H₂ selectivity and CO conversion of the CuO-ZnO/Al₂O₃ catalysts prepared by CP, DP, DP-Ultra, IWI, CP-Urea, and IWI-Urea methods at 180°C with a feed flow rate of 150, 30, and 120 mL/min of N₂, CO, and H₂O, respectively.

Catalyst code	H ₂ Selectivity (%)	CO conversion (%)
CP	93	33
DP	95	6.6
DP-Ultra	90	5.3
IWI	94	1.3
CP-Urea	95	39
IWI-Urea	97	47
Commercial CuO-ZnO/Al ₂ O ₃	99	8.8

Table 4: CO conversions of Response Surface Methodology (RSM) design of experiments of the CuO-ZnO/Al₂O₃ catalysts prepared by IWI-Urea method.

NO.	Temperature (°C)	H ₂ O/CO Ratio	Space Velocity (1/h)	CO Conversion%
1	150	4	30000	43
2	200	8	25000	62
3	250	8	30000	72
4	150	6	35000	50
5	200	4	25000	70
6	200	4	35000	89
7	150	6	25000	33
8	150	8	30000	53
9	250	4	30000	82
10	200	8	35000	85
11	200	6	30000	68
12	250	6	25000	78
13	250	6	35000	97
14	200	6	30000	67
15	200	6	30000	68

Table 5: Analysis of Variance for CO Conversion versus Temperature, H₂O/CO Ratio, Space Velocity.

Source	DF	Seq SS	Adj MS	F	P
Regression	3	6615.00	2205.00	44.87	0.000
Linear	3	6615.00	2205.00	44.87	0.000
Temperature	1	6050.00	6050.00	123.10	0.000
Space Velocity	1	420.50	420.50	8.56	0.014
H ₂ O/CO Ratio	1	144.50	144.50	2.94	0.114
Residual Error	11	540.60	49.15	-	-
Total	14	7155.60	-	-	-

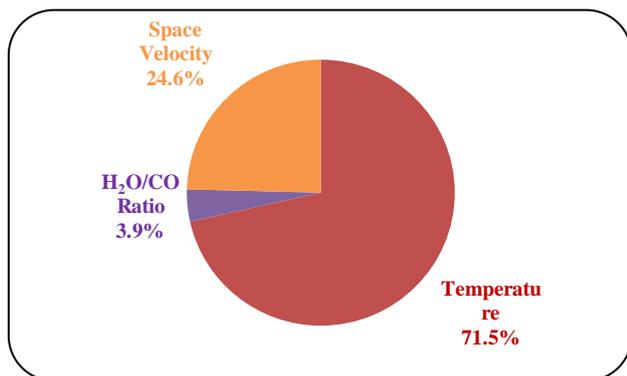


Fig. 6: Contribution of each factor's effect on CO conversion of the CuO-ZnO/Al₂O₃ catalysts prepared by IWI-Urea method.

In the first stage, there is an equilibrium-limited reaction at high temperatures (above 350 °C) and with increasing temperature, equilibrium CO conversion decreases. In the second stage, there is usually kinetically limited at low temperatures (below 250 °C)[48]. Over the range of conditions employed in this study, increasing the temperature caused to improve reaction kinetics and increase CO conversion.

According to Fig. 7b, the highest CO conversion was obtained at the maximum temperature of 250°C and steam to CO ratio of 4. The steam to CO ratio could not be regarded as a more significant factor than the other factors, but in general, if this ratio is too low, the catalyst activity would decrease due to a decrease in the concentration of one of the reactants, resulting in a low CO conversion. On the other hand, high steam to CO ratio would lead to competitive adsorption of water and CO, with preferential adsorption of water. Therefore, an optimal value for this factor needs to be defined. At the high temperature of 250°C, the highest CO conversion was obtained at the lowest steam to CO ratio of 4. For temperatures as low as 150°C, however, the optimal steam to CO ratio was approximately 5 to 6. Fig. 7c illustrates the simultaneous effect of steam to CO ratio and space velocity on CO conversion. Although the steam to CO ratio had the least effect on CO conversion compared with the other factors, higher CO conversions were generally obtained at lower steam to CO ratios.

CONCLUSIONS

This study shows that the IWI-Urea preparation method for a CuO-ZnO/Al₂O₃ catalyst results in the highest activity for the catalyst compared with the other

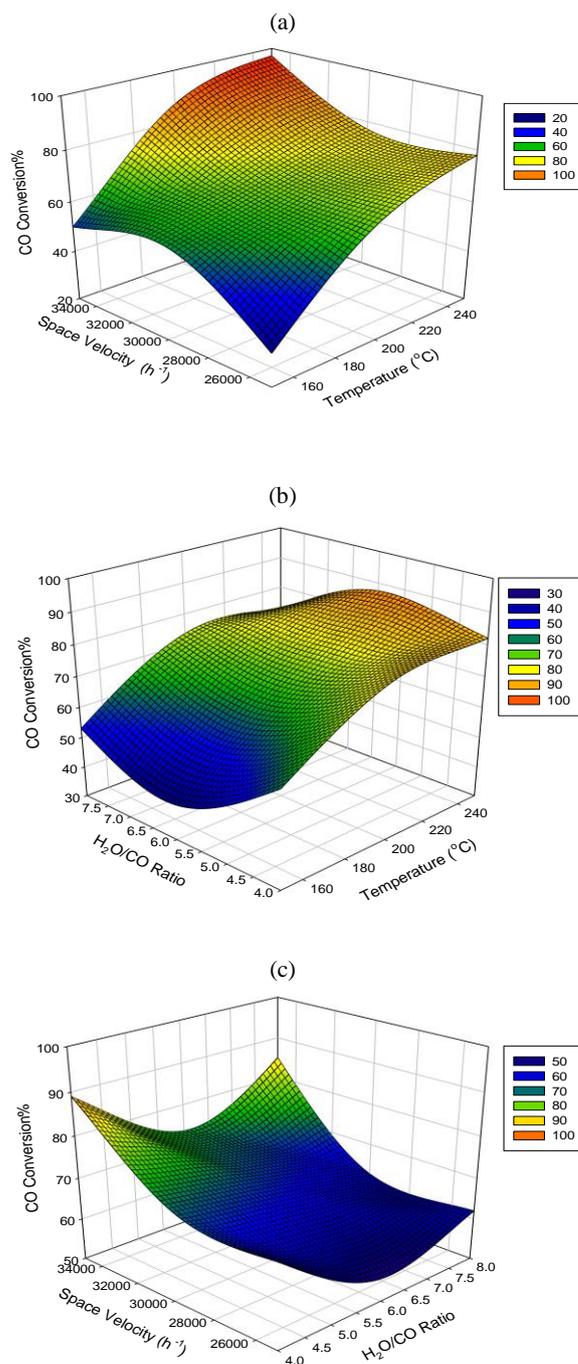


Fig. 7. 3-D diagram of the CuO-ZnO/Al₂O₃ catalysts prepared by IWI-Urea method for the simultaneous effects of temperature and space velocity on CO conversion (a), temperature and steam to CO ratio on CO conversion (b), and steam to CO ratio and space velocity on CO conversion (c).

preparation methods employed here. According to the XRD spectra, the intensity of the CuO phase peaks for the sample prepared by IWI-Urea method was more

than other samples. The peak shapes revealed that despite not being very small, the particles turned out to be nano-sized.

SEM pictures confirmed the XRD results, as the dispersion and homogeneity of the particles were easily distinguishable in these pictures. The sample prepared by IWI-Urea method had the finest particle homogeneity.

In DP, DP-Urea, and IWI methods, the size of the recognizable particles in SEM pictures was extremely small. These small particles would lead to unfavorable results in wet environments because in the competition between water and CO adsorption, the water adsorption on these sites would be stronger, leading to a decrease in catalyst activity. The deposition-precipitation-based synthesis methods led to the highest specific surface area and pore volume. The co-precipitation-based methods resulted in the lowest highest specific surface area and pore volume.

Over the range of experimental conditions employed in this study, the optimum condition for the highest CO conversion (97%) was obtained at the reaction temperature of 250 °C, steam to CO ratio of 4, and gas space velocity of 35000 $1/h$.

In terms of the gas space velocity effect on CO conversion, it was observed that at low reaction temperatures, the lower gas space velocity results in the higher CO conversions. While at high reaction temperatures, the higher gas space velocity results in the higher CO conversions. From the standpoint of steam to CO ratio's effect on the CO conversion, the results showed that at higher reaction temperatures, the lower steam to CO ratio leads to the higher CO conversion. And at low reaction temperatures, an optimal value for steam to CO ratio exists for the highest CO conversion. Finally, at a constant reaction temperature, the lower steam to CO ratios leads to the higher CO conversions.

Acknowledgements

The financial support of the Iran National Science Foundation (INSF), contract no. 91/S/23551, is gratefully acknowledged.

Received : Jun. 21, 2022 ; Accepted : Sep. 26, 2022

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