

Ga-doped CeO_2 solid solutions as promoters for Cu-based catalysts: Enhancing CO_2 hydrogenation to methanol via optimized metal–support interaction

Tuo Guo^{1,2} | Wenwen Liu¹ | Panpan Yang³ | Qingjie Guo^{1,3}  | Pei Sean Goh⁴

¹Center of Carbon Capture and Industrial Utilization, Jiangmen Laboratory of Carbon Science and Technology, Jiangmen, China

²Xinyuan Green Carbon Technology (Jiangmen) Co., Ltd, Jiangmen, China

³State Key Laboratory of Coal Efficient Utilization and Green Chemical Engineering, College of Chemistry and Chemical Engineering, Ningxia University, Yinchuan, China

⁴Advanced Membrane Technology Research Centre (AMTEC), Universiti Teknologi Malaysia (UTM), Skudai, Malaysia

Correspondence

Qingjie Guo, Center of Carbon Capture and Industrial Utilization, Jiangmen Laboratory of Carbon Science and Technology, Jiangmen, 529020, China.
Email: qingjie_guo@vip.sina.com

Funding information

Natural Science Foundation Project of Ningxia, Grant/Award Number: 2022AAC01001; National Foreign Experts Program, Grant/Award Number: H20240298

Abstract

The low methanol selectivity of Cu/ CeO_2 in CO_2 hydrogenation stems from weak metal–support interaction (MSI) and dominant reverse water gas shift (RWGS) pathways. Ga-doped CeO_2 solid solutions are proposed to enhance MSI and oxygen vacancies, addressing insufficient CO_2 activation and H_2 dissociation in conventional Cu-based catalysts. $\text{CuO-CeGa}_x\text{O}_x$ ($y = 0-0.3$) catalysts were synthesized via co-precipitation. Structural and catalytic properties were analyzed by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), temperature-programmed H_2 reduction (H_2 -TPR), temperature-programmed desorption of adsorbed CO_2 (CO_2 -TPD), and transmission electron microscopy (TEM). Ga doping ($y = 0.2$) optimized CeGaO_x solid solution formation, achieving the highest specific surface area ($142 \text{ m}^2/\text{g}$), and Cu^0 content (73.4%). At 260°C , $\text{CuO-CeGa}_{0.2}\text{O}_x$ showed 12.6% X_{CO_2} , 57% $S_{\text{CH}_3\text{OH}}$, and $\text{STY} = 308.8 \text{ g}_{\text{MeOH}} \text{ Kgcat}^{-1} \text{ h}^{-1}$. Enhanced oxygen vacancies and moderate basic sites suppressed RWGS, favouring methanol pathways. Stability tests confirmed 180 h performance retention without structural degradation. Ga doping strengthens MSI via CeGaO_x solid solutions, promoting oxygen vacancies and Cu^0 dispersion. This dual optimization enhances CO_2 adsorption, H_2 dissociation, and methanol selectivity while suppressing CO byproducts. The $\text{CuO-CeGa}_{0.2}\text{O}_x$ catalyst demonstrates industrial potential, offering a design strategy for high-performance CO_2 hydrogenation catalysts.

KEYWORDS

CeGaO_x , CO_2 , Cu-based catalysts, metal–support interaction, methanol

1 | INTRODUCTION

With the development of modern industrialization, the concentration of CO_2 in the global atmosphere has continued to rise, causing serious impacts on the ecological environment.^[1] Converting CO_2 into fuels and various chemicals is an effective way to achieve carbon neutrality and reduce the greenhouse effect, and it has received widespread attention.^[2,3] CO_2 , a renewable and non-toxic

C1 feedstock, offers a sustainable alternative to fossil-derived chemicals. Its catalytic conversion enables the synthesis of value-added products, including some chemical intermediates such as CO,^[4] methanol,^[5] light olefins,^[6] and dimethyl ether.^[7] Among the many CO_2 derivatives, methanol, as an important chemical product and excellent green fuel, has received extensive research. The development of robust catalysts with high CO_2 conversion and methanol selectivity is pivotal for

industrial-scale CO₂ valorization.^[8,9] Currently, the CuO-ZnO-Al₂O₃ catalyst used in industry has low CO₂ conversion and CH₃OH selectivity, poor stability, and many by-products.^[10,11] Therefore, the development of new Cu-based catalysts with high activity and stability has become a hot spot and challenge in this field of research.

Among various metal oxides, CeO₂ is considered a promising support due to its excellent redox ability, which enables it to form strong interactions with Cu and exhibit good stability.^[12,13] However, the Cu/CeO₂ binary catalyst exhibits low CO₂ selectivity in the hydrogenation of CO₂ to methanol, primarily because CO₂ hydrogenation proceeds mainly through the reverse water gas shift (RWGS) reaction pathway at the Cu/CeO₂ interface. Moreover, Cu has weak adsorption capacity for CO results in the generation of a large amount of CO by-products, and the yield of methanol through further hydrogenation of CO is low.^[14,15] Consequently, the moderate CO₂ conversion rate of the Cu/CeO₂ binary catalyst does not meet the requirements for industrial applications. Wang et al.^[12,16,17] found through studies on Cu/ZrCeO₂ catalysts that the interaction between Cu and the cerium zirconium solid solution favours further hydrogenation of carbon-containing adsorbed species and enhances the hydrogenation rates of formate (HCOO*) and methoxy (*OCH), thereby promoting methanol production. Nie et al.^[18] also reported that the strong metal-support interaction (MSI) formed between Cu and the manganese cerium solid solution helps increase the number of Cu⁰ and Ce³⁺ species, facilitating the synthesis of methanol from CO₂ via the formate pathway. Thus, the strong interaction between the metal (Cu) and the solid solution is crucial for promoting CO₂ hydrogenation to methanol. According to reports, Ga³⁺ can substitute Ce⁴⁺ in CeO₂ to form CeGa_yO_x solid solutions, which facilitate the conversion of Ce⁴⁺ to Ce³⁺, generating moderate oxygen vacancies and exhibiting stronger hydrogen dissociation ability.^[19,20] These CeGa_yO_x solid solutions also possess good stability and redox ability, enabling strong interactions with active components, thereby benefiting methanol synthesis. However, the mechanism by which the strong MSI between Cu and CeGa_yO_x solid solutions enhances the selectivity of CO₂ hydrogenation to methanol remains unexplored.

This paper introduces a CuO/Ga_yCeO_x ($y = 0, 0.1, 0.2, 0.25, 0.3$) catalyst prepared by a co-precipitation method. To unravel the structure-activity relationship, temperature-programmed H₂ reduction (H₂-TPR) was utilized to probe Cu reducibility modulated by GaCeO_x support, while CO₂-TPD quantified basic site distribution critical for CO₂ activation. X-ray photoelectron spectroscopy (XPS) and high-resolution-transmission electron microscopy (HR-TEM) further correlated oxygen vacancy density with Cu⁰ dispersion, directly linking MSI strength to methanol selectivity.

2 | MATERIALS AND METHODS

2.1 | Catalyst preparation

The CuO-CeGa_yO_x ($y = 0, 0.1, 0.2, 0.3$) ternary catalysts were prepared via the coprecipitation method. A certain amount of Cu(NO₃)₂·3H₂O, Ce(NO₃)₃·6H₂O, and Ga(NO₃)₃·xH₂O (where Ga represents a molar fraction of y in the catalyst, and Cu and Ce together represent a molar fraction of $(1-y)/2$ in the catalyst) were weighed and dissolved in an appropriate amount of deionized water with heating and stirring until a complete solution was formed, denoted as Solution A. Separately, a certain amount of NaOH was dissolved in deionized water to form a 1 mol/L NaOH solution, denoted as Solution B. A beaker containing 50 mL of deionized water was heated and stirred in a 70°C water bath, denoted as Solution C. A peristaltic pump was used to simultaneously drip Solution A and Solution B into Solution C, maintaining the system's pH at 8 until Solution A was completely added. Heating and stirring were continued for 2 h, followed by natural cooling and aging for 2 h at rest. Vacuum filtration was performed, and the precipitate was repeatedly washed with deionized water and methanol to remove excess Na⁺. The filtered precipitate was dried overnight in an oven at 80°C. The dried powder was then placed in a muffle furnace and heated to 400°C at a rate of 5°C/min, followed by calcination in air for 4 h. After calcination, the catalyst was pressed, sieved to 40–60 mesh under a pressure of 20 MPa, and set aside for use.

2.2 | Evaluation of catalyst activity

The catalytic activity of CuO-CeGa_yO_x in the CO₂ hydrogenation to methanol was measured in a high-pressure fixed bed (Figure S1). After weighing 0.3 g of 60–80 mesh catalyst and 0.6 g of 40–60 mesh quartz sand, the two were mixed and filled into the heated section of a 5 mm diameter reaction tube. After filling, the gas tightness was checked. Firstly, H₂ was introduced for pre-reduction at 300°C for 2 h. Then, under a mixed gas atmosphere of 75% H₂ + 25% CO₂, the reaction was conducted at a pressure of 5 MPa, a gas hourly space velocity (GHSV) of 12,000 mL · g⁻¹ · h⁻¹, and various reaction temperatures ($T = 220^{\circ}\text{C}, 240^{\circ}\text{C}, 260^{\circ}\text{C}, 280^{\circ}\text{C}, 300^{\circ}\text{C}$) for 6 h. The reaction products were heated to 110°C and then directly fed into a gas chromatograph (Agilent GC8890) for analysis. The components and their contents were determined based on the retention times and peak areas of each component gas in the column. The content of the product was also determined by the retention times and peak areas of the component gases in the column. The CO₂ conversion rate (X_{CO_2}), methanol selectivity ($S_{\text{CH}_3\text{OH}}$), CO

selectivity (S_{CO}), and space-time yield (STY) were calculated using Equations (1)–(4).

$$X_{CO_2} = \frac{f_{CO}A_{CO} + i(f_{CH_4}A_{CH_4} + f_{CH_3OH}A_{CH_3OH})}{f_{CO_2}A_{CO_2} + f_{CO}A_{CO} + i(f_{CH_4}A_{CH_4} + f_{CH_3OH}A_{CH_3OH})} \quad (1)$$

$$S_{CH_3OH} = \frac{i \times f_{CH_3OH}A_{CH_3OH}}{f_{CO}A_{CO} + i(f_{CH_4}A_{CH_4} + f_{CH_3OH}A_{CH_3OH})} \quad (2)$$

$$S_{CO} = \frac{f_{CO}A_{CO}}{f_{CO}A_{CO} + i(f_{CH_4}A_{CH_4} + f_{CH_3OH}A_{CH_3OH})} \quad (3)$$

$$STY = \frac{GHSV}{22.4} \times V\%(CO_2) \times X(CO_2) \times S(CH_3OH) \times M_{CH_3OH} \quad (4)$$

The transformation factor i is calculated by Equation (5).

$$i = \frac{f_{CH_4-TCD}A_{CH_4-TCD}}{f_{CH_4-FID}A_{CH_4-FID}}, \quad (5)$$

where A is the peak area, f is the correction factor for each gas component, GHSV is the feed gas velocity in the reactor, V is the proportion of CO_2 in the feed gas, and M_{CH_3OH} is the unit molar mass of methanol.

2.3 | Catalyst characterization

X-ray diffraction (XRD) using a Bruker D8 Advance (Germany) type diffractometer with $CuK\alpha$ radiation, an intra-tube voltage of 40 kV, a tube current of 40 mA, a scan rate of $8^\circ/\text{min}$, and a scan range of $2\theta = 10\text{--}85^\circ$. Here, $K = 0.89$ (shape factor), $\lambda = 0.15418 \text{ nm}$ ($Cu K\alpha$ radiation), β is the full width at half maximum (FWHM) of the CuO (111) peak, and θ is the Bragg angle.

The specific surface area of the catalysts was calculated using a Conta Autosorb IQ fully automated physisorption apparatus with N_2 adsorbent and a sample degassed at 250°C for 6 h. The specific surface area was calculated by the Brunauer–Emmett–Teller (BET) equation and the pore volume and pore size by the Barrett–Joyner–Halenda model.

Via scanning electron microscopy (SEM) the apparent morphology of the catalyst was determined using a JSM-7500F, Japan field emission scanning electron microscope. Prior to scanning, the specimens were placed on a conductive adhesive, then sprayed with gold and the specimens were scanned at an accelerating voltage of 10 kv.

Transmission electron microscopy (TEM) was conducted using a JEOL JEM-F200, Japan. The sample was dispersed in ethanol solution for sonication, then a few drops of the suspension were placed on a copper grid and dried, accelerated at 200 kV, energy spectrum model JED-2300 T, and high-resolution morphology was taken.

X-ray photoelectron spectroscopy (XPS) was performed using an ESCALAB 250 X-ray photoelectron spectrometer from Thermo Scientific, USA, under the following conditions: the Al K Alpha ray (15 kV, 150 W, $h\nu = 1486.60 \text{ eV}$) was used as the excitation source and the catalyst was corrected for charge effects with contaminated carbon C 1 s (284.6 eV) for the binding energy corrected for charge effects.

Temperature-programmed H_2 reduction (H_2 -TPR) was carried out using an AutoChem II 2920 fully automated temperature rise chemisorption instrument. The test conditions were as follows: 30–40 mg of catalyst was weighed, purged with He (50 mL/min) for 1 h, cooled to 500°C , and desorbed to 700°C in a 10% H_2 /Ar gas stream at a temperature rise of $10^\circ\text{C}/\text{min}$, and the reducing gas was detected by a thermal conductivity detector (TCD).

Temperature-programmed desorption of adsorbed CO_2 (CO_2 -TPD) was also determined using a fully automated AutoChem II 2920 chemisorber. The sample was first reduced with 30% H_2 at 260°C for 6 h, then purged with He gas (50 mL/min) for 1 h. A mixture of 10% CO_2 /He (30 mL/min) was introduced for 1 h until saturation, and finally the sample was desorbed at a rate of $10^\circ\text{C}/\text{min}$ to 700°C under He gas.

3 | CHARACTERIZATION OF $CuO\text{-}CeGa_yO_x$ CATALYST

3.1 | The structure of $CuO\text{-}CeGa_yO_x$ catalyst

The XRD patterns of fresh $CuO\text{-}CeGa_yO_x$ ($y = 0, 0.1, 0.2, 0.3$) catalysts are shown in Figure 1A. It can be observed from the figure that the diffraction peaks at $2\theta = 28.6^\circ, 33.1^\circ, 47.5^\circ$, and 56.3° are attributed to the diffraction peaks of fluorite-structured CeO_2 (PDF#34-0394). The diffraction peaks of CuO (PDF#48-1548) appear at $2\theta = 35.6^\circ$ and 38.7° , while no obvious GaO_x diffraction peaks are found in the spectra. Furthermore, after doping GaO_x into the $CuO\text{-}CeO_2$ catalyst, the 2θ of the CeO_2 diffraction peaks on the fresh $CuO\text{-}CeGa_yO_x$ catalysts shift to higher angles. With the increase in Ga species content, the degree of CeO_2 diffraction peak shift gradually increases. This obvious shift is caused by the smaller Ga ions entering the CeO_2 lattice, leading to a decrease in the lattice parameter a of the catalyst (Table 1), demonstrating the formation of $CeGaO_x$ solid

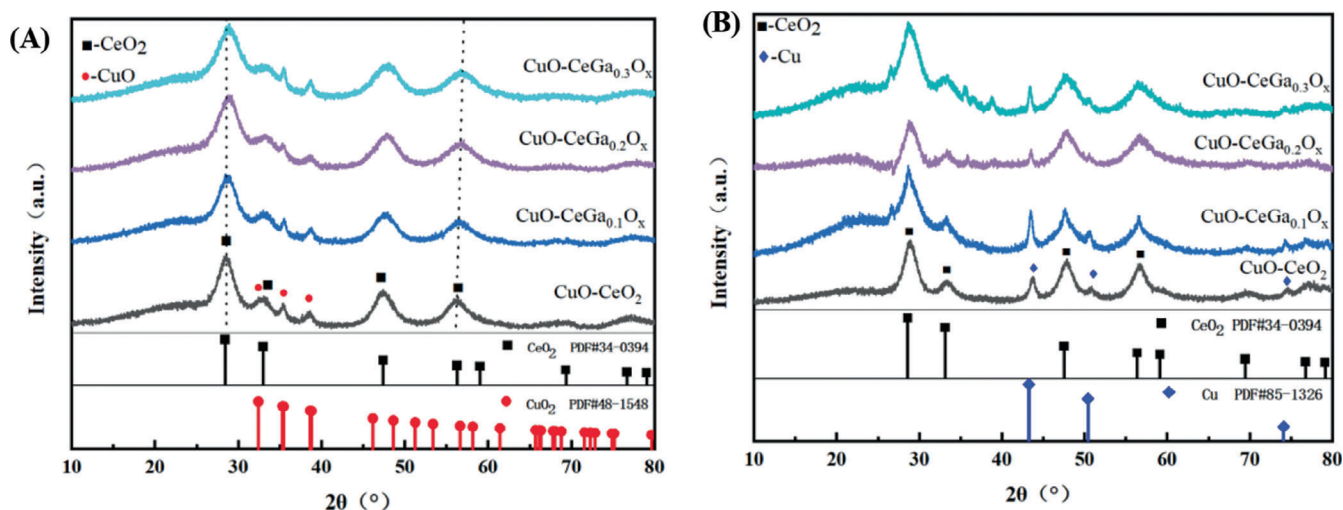


FIGURE 1 X-ray diffraction (XRD) patterns of (A) fresh and (B) reduced CuO-CeGa_yO_x catalysts.

Sample	S _{BET} (m ² ·g ⁻¹)	Pore diameter (nm)	Pore volume (cm ³ ·g ⁻¹)	Cell parameter
CuO-CeO ₂	126.81	16.57	0.48	5.407
CuO-CeGa _{0.1} O _x	139.14	14.29	0.45	5.393
CuO-CeGa _{0.2} O _x	142.19	17.04	0.57	5.382
CuO-CeGa _{0.3} O _x	132.13	14.67	0.43	5.403

Abbreviation: S_{BET}, specific surface area.

TABLE 1 Structure and lattice parameters of CuO-CeGa_yO_x CuO-CeGa_yO_x (y = 0, 0.1, 0.2, 0.3) catalysts.

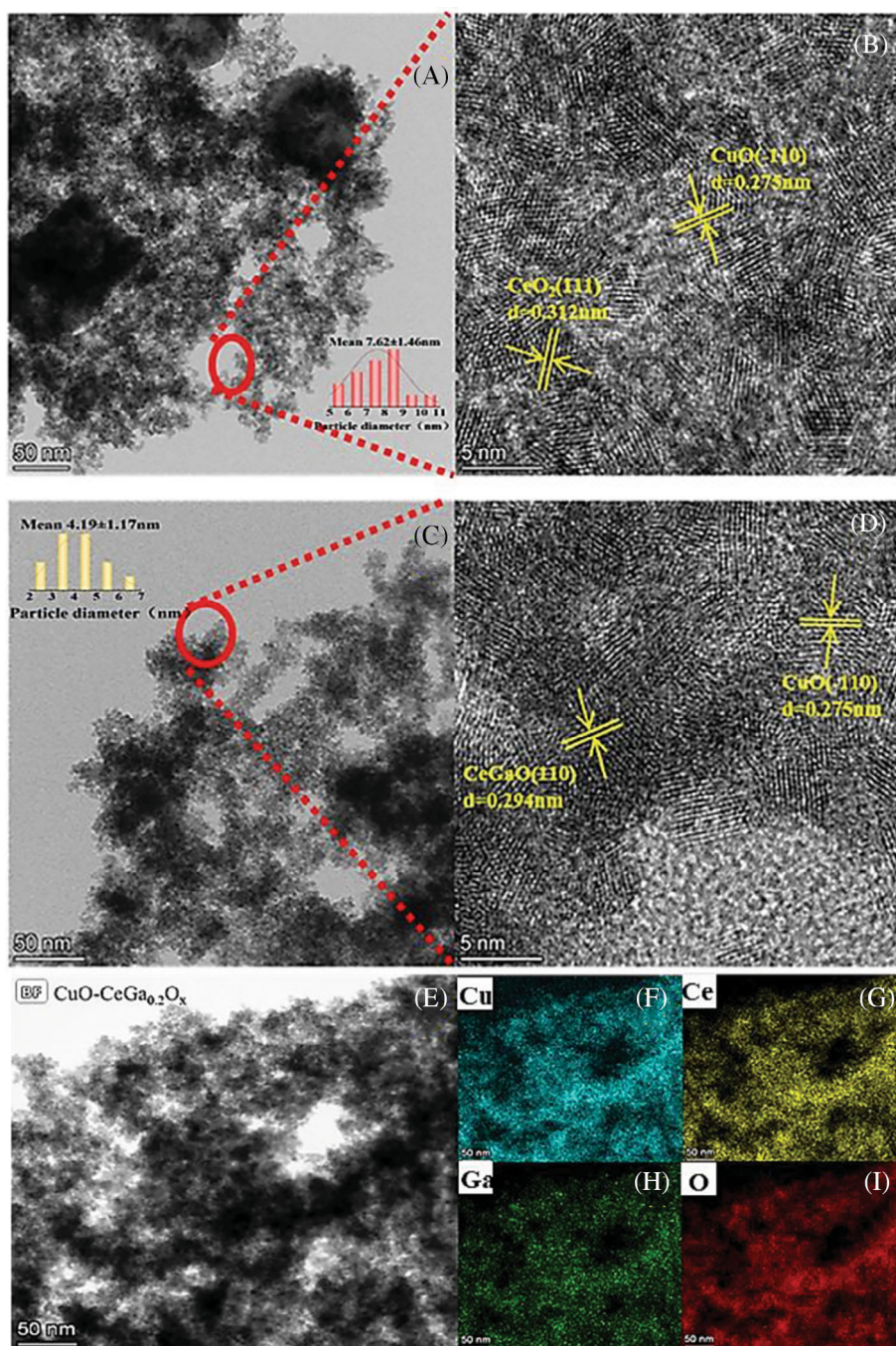
solution in the catalyst.^[20,21] When the content of Ga species is about 20%, the deviation degree of CeO₂ diffraction peak reaches the maximum. As the content of Ga species continues to increase, the deviation degree of CeO₂ diffraction peak begins to gradually decrease, while the unit cell parameter α value increases, indicating that the continued increase in the content of Ga species cannot continue to increase the solid solution content. The CuO-CeGa_{0.2}O_x catalyst has the largest number of solid solutions.

The XRD patterns of CuO-CeGa_yO_x catalysts after hydrogen reduction are shown in Figure 1. From the figure, diffraction peaks of Cu (PDF#85-1326) appear at $2\theta = 43.3^\circ$ and 50.4° , corresponding to the (111) and (200) crystal planes of Cu, respectively.^[22] In all samples, the diffraction peaks of CuO disappear, indicating that the reduction at 300°C for 3 h can effectively reduce CuO in CuO-CeGa_yO_x catalysts to metallic Cu. After reduction, CeO₂ remains in its oxidized state, mainly due to the higher reduction temperature of CeO₂. Furthermore, the intensity of Cu diffraction peaks in the reduced CuO-CeGa_{0.2}O_x catalyst is significantly reduced, with weakened crystallinity, indicating that Cu can be better dispersed on the CeGa_{0.2}O_x solid solution, thereby inhibiting the growth of metallic Cu particles during the reduction process of the catalyst.^[18,23]

The microstructures of CuO-CeO₂ and CuO-CeGa_{0.2}O_x catalysts were studied using TEM. As is depicted in Figure 2A, the average particle size of the metal particles in the CuO-CeO₂ catalyst is 7.62 nm. The morphology of the CuO-CeGa_{0.2}O_x catalyst shown in Figure 2B does not change significantly, but the average particle size of the metal in the Ga-doped catalyst changes to 4.19 nm, indicating that the doping of Ga helps to inhibit the agglomeration of CuO grains and facilitates the dispersion of Cu species in the catalyst. Figure 2C indicates lattice fringes of the CuO(110) crystal plane and CeO₂(111) crystal plane can be observed in the HR-TEM image of the CuO-CeO₂ catalyst. Figure 2D demonstrates the HR-TEM image of the CuO-CeGa_{0.2}O_x catalyst, lattice fringes of the CuO(110) crystal plane and CeGaO_x(110) crystal plane can be observed simultaneously, indicating the successful preparation of CeGaO_x solid solution. Figures 2F-K and S2 show the energy dispersive spectrometer (EDX) mapping distribution of CuO-CeO₂ and CuO-CeGa_{0.2}O_x catalysts, respectively. It can be seen that Cu, Ce, and O elements are uniformly distributed in CuO-CeO₂; and Ga, Cu, Ce, and O elements are uniformly distributed in CuO-CeGa_{0.2}O_x catalysts.

Figure 3 presents the SEM images of CuO-CeGa_yO_x catalysts. The morphology of all catalysts exhibits

FIGURE 2 (A) Transmission electron microscopy (TEM) images of CuO/CeO₂ catalyst; (B) High-resolution transmission electron microscopy (HR-TEM) images of CuO/CeO₂ catalysts; (C) TEM images of CuO-CeGa_{0.2}O_x catalyst; (D) HR-TEM images of CuO-CeGa_{0.2}O_x catalyst; (E) TEM images of CuO-CeGa_{0.2}O_x catalyst; (F–G) Energy dispersive spectrometer (EDX) elemental mapping of CuO-CeGa_{0.2}O_x catalysts (blue—Cu, yellow—Ce, green—Ga, red—O).



irregular granular shapes, and the introduction of Ga does not significantly alter the morphology of CuO-CeO₂. Figure 3A indicates that CuO-CeO₂ exhibits clear agglomeration. Figure 3B,C demonstrate that the introduction of an appropriate amount of Ga can alleviate the agglomeration of the catalyst, leading to a significant increase in the dispersion between particles. When the Ga content is 20%, the particle dispersion is optimal, accompanied by abundant pore structures, which facilitate the dispersion of active sites. In contrast, Figure 3D shows that excessive introduction of Ga can lead to the agglomeration of the catalyst. The N₂-adsorption and

desorption isotherms of the CuO-CeGa_yO_x catalysts after calcination are depicted in Figure S3. According to the IUPAC classification criteria, all the catalysts exhibit type IV isotherms characterized by H3 hysteresis loops, indicating that they possess mesoporous structures with uniform pore size distributions.^[24] The lattice and structural parameters of the CuO-CeGa_yO_x catalysts are summarized in Table 1. Compared to the CuO-CeO₂ catalyst, the CuO-CeGa_yO_x catalysts show significant improvements in both specific surface area and pore volume. Among them, the CuO-CeGa_{0.2}O_x catalyst exhibits the highest S_{BET} (142.19 m² · g⁻¹) and pore volume (0.57 cm³ · g⁻¹).

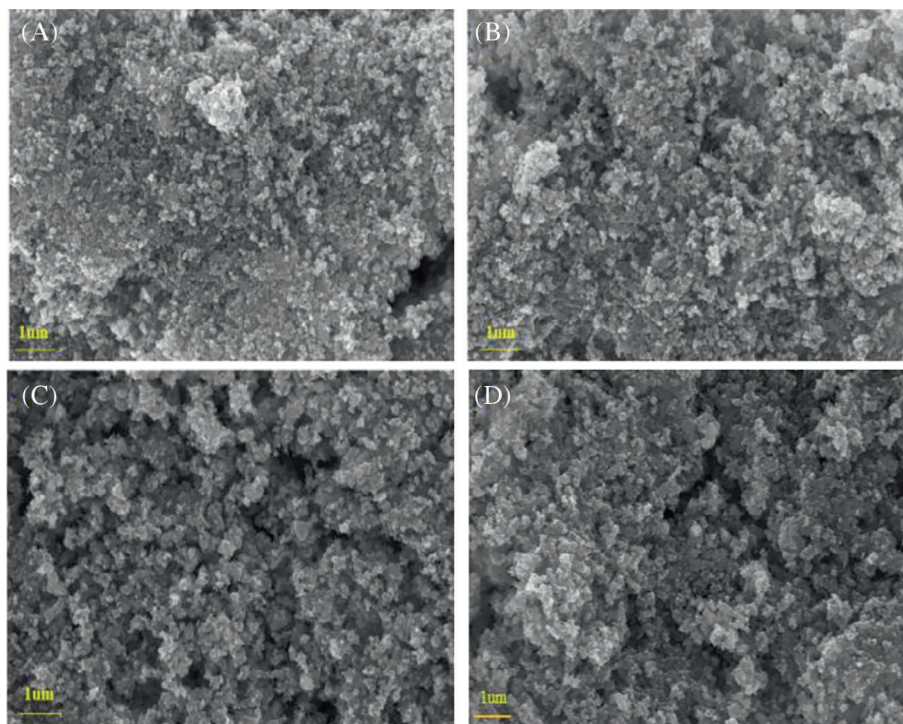


FIGURE 3 Scanning electron microscopy (SEM) images of (A) CuO-CeO₂, (B) CuO-CeGa_{0.1}O_x, (C) CuO-CeGa_{0.2}O_x, and (D) CuO-CeGa_{0.3}O_x catalysts.

SEM analysis reveals that an appropriate amount of Ga doping can reduce catalyst agglomeration, thereby enhancing the S_{BET} and pore volume. However, when the Ga content in the catalyst is further increased, the S_{BET} and pore volume begin to decrease. For instance, the CuO/Ga_{0.3}CeO_x catalyst has a reduced S_{BET} of 133.13 m² · g⁻¹ and a pore volume of only 0.43 cm³ · g⁻¹. This is attributed to excessive Ga loading, which can lead to catalyst agglomeration and pore blockage. A larger S_{BET} and pore volume are beneficial for exposing more Cu⁰ catalytic active sites, thereby enhancing the ability of the catalyst to adsorb and dissociate H₂.^[1]

3.2 | Reduction performance of CuO-CeGa_yO_x catalyst

Figure 4 explores the reduction behaviour of CuO-CeGa_yO_x ($y = 0, 0.1, 0.2, 0.3$) catalysts through H₂-TPR. The CuO-CeO₂ catalyst exhibits a single reduction peak between 250 and 320°C, representing the reduction of CuO to Cu. After adding Ga, a shoulder peak appears on its main reduction peak, where the α peak is attributed to the highly dispersed CuO species with small grains on the catalyst surface, and the β peak is attributed to the reduction of bulk CuO species with large grains.^[25,26] The reduction temperature of CuO/Ga_yCeO_x catalysts first decreases and then increases with the increase in Ga content. Because the interaction between Cu and GaCeO_x solid solution promotes the dispersion of CuO,

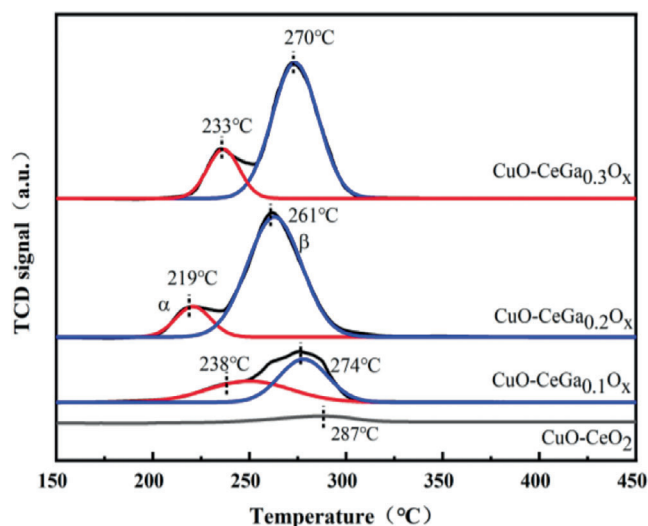


FIGURE 4 Temperature-programmed H₂ reduction (H₂-TPR) curves of CuO-CeGa_yO_x catalysts.

transforming the large bulk CuO particles into highly dispersed small CuO particles, thereby reducing the required reduction temperature. Excessive introduction of Ga can lead to catalyst agglomeration, inhibiting the dispersion of active components and increasing the reduction temperature. When the Ga content in the catalyst is 20%, the reduction temperature of the α peak reaches a minimum of 219°C, indicating the strongest interaction between Cu and GaCeO_x solid solution in the CuO/Ga_{0.2}CeO_x catalyst. Furthermore, the interaction

between Cu and GaCeO_x solid solution in the catalyst is beneficial to improving the reduction performance of the catalyst.

3.3 | Adsorption performance of CuO-CeGa_yO_x catalyst

To investigate the adsorption characteristics of CO₂ on the reduced CuO/Ga_yCeO_x ($y = 0, 0.1, 0.2, 0.3$) catalysts, CO₂-TPD experiments were performed. As shown in Figure 5, all catalysts contain a certain number of basic sites, indicating that all catalysts have a certain adsorption capacity for CO₂. The CO₂-TPD curve of the CuO/CeO₂ catalyst exhibits only one broad CO₂ desorption peak, while the CO₂-TPD curves of CuO/Ga_yCeO_x catalysts show two CO₂ desorption regions. The CO₂ desorption peak appearing in the range of 50–200°C is attributed to the carbon species adsorbed on the weakly basic sites of the catalysts, which are generally considered to be related to the hydroxyl groups on the catalyst surface. The moderately strong basic sites between 200 and 550°C correspond to the presence of metal–oxygen pairs.^[27,28] The fact that the CuO/CeO₂ catalyst has only one broad CO₂ desorption peak indicates its weaker CO₂ adsorption capacity, which may be related to the lower methanol selectivity exhibited by the CuO/CeO₂ catalyst. Compared with the CuO/CeO₂ catalyst, the strong interaction between Cu species and GaCeO_x solid solution in CuO/Ga_yCeO_x catalysts results in more moderately strong basic sites in the catalysts, indicating that the interaction between Cu species and GaCeO_x solid solution nanorods enhances the CO₂ adsorption

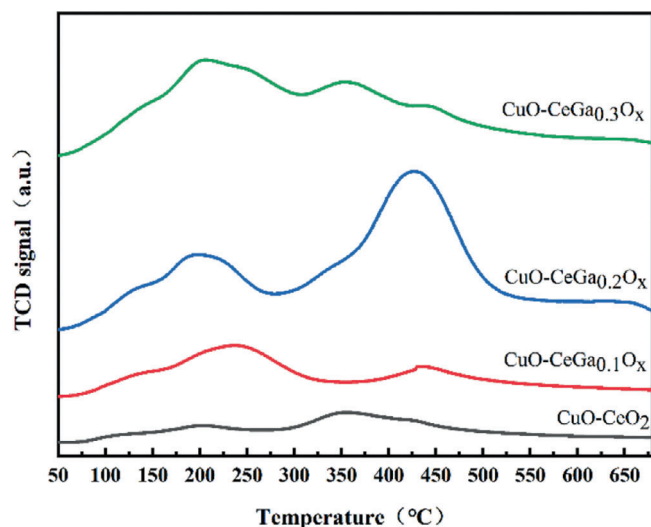


FIGURE 5 Temperature-programmed desorption of adsorbed CO₂ (CO₂-TPD) curves of CuO-CeGa_yO_x catalysts.

capacity of the catalysts. However, an excessively high concentration of Ga loading can generate coverings on the catalyst surface, concealing the basic sites and thereby reducing the number of active centres. Among them, the CuO/Ga_{0.2}CeO_x catalyst has the highest concentration of moderately strong basic sites and the most total basic sites, and moderately strong sites are closely related to methanol selectivity,^[23,29,30] which may lead to the best methanol selectivity of the CuO/Ga_{0.2}CeO_x catalyst.

3.4 | Oxygen vacancies and valence states of CuO/Ga_yCeO_x catalysts

Figure 6 shows the XPS spectra of CuO-CeGa_yO_x ($y = 0, 0.1, 0.2, 0.3$) catalysts after H₂ reduction. As shown in Figure 6A, the Cu 2p spectra of CuO-CeGa_yO_x catalysts after hydrogen reduction reveal that Cu⁰ species are the dominant copper species in these catalysts. Table 2 lists the Cu⁰ content of CuO-CeGa_yO_x catalysts, indicating that the CuO-CeGa_{0.2}O_x catalyst has the highest Cu⁰ species content (73.41%), which is closely related to the excellent reduction performance of the CuO-CeGa_{0.2}O_x catalyst. Figure 6B displays the XPS spectral profiles of Ce 3d regions in reduced CuO-CeGa_yO_x ($y = 0, 0.1, 0.2, 0.3$) catalyst systems. Characteristic peaks observed at V, V'', V'', U, U'', and U'' correspond to Ce 3d_{3/2}, which are related to the spin-orbit doublets and represent Ce⁴⁺. Figure 6B,C, along with Table 2, demonstrate that the trend of defective oxygen concentration on CuO/CeGa_yO_x catalysts is consistent with the trend of Ce³⁺/(Ce³⁺+Ce⁴⁺) ratio. The addition of different amounts of Ga species to the catalysts increases the concentration of Ce³⁺ species, and the CuO/Ga_{0.2}CeO_x catalyst contains the highest concentration of Ce³⁺ species. The transformation of Ce⁴⁺ species to Ce³⁺ species leads to charge imbalance and the generation of oxygen vacancies on the catalyst surface, thereby enhancing the surface defective oxygen concentration. The substitution of Ga ions for cerium ions to form a solid solution increases the concentration of Ce³⁺ species, which affects the oxygen vacancy concentration. Oxygen vacancies are beneficial for the formation of MSIs between Cu and GaCeO_x solid solutions,^[30] and they also contribute to the adsorption and activation of CO₂ on the surface of CuO/Ga_{0.2}CeO_x catalysts,^[31] as well as enhancing the stability of intermediates in the methanol synthesis reaction from CO₂ hydrogenation.^[32] The CuO/Ga_{0.2}CeO_x catalyst, with the largest number of solid solutions and the highest concentration of oxygen vacancies, exhibits the best catalytic performance.

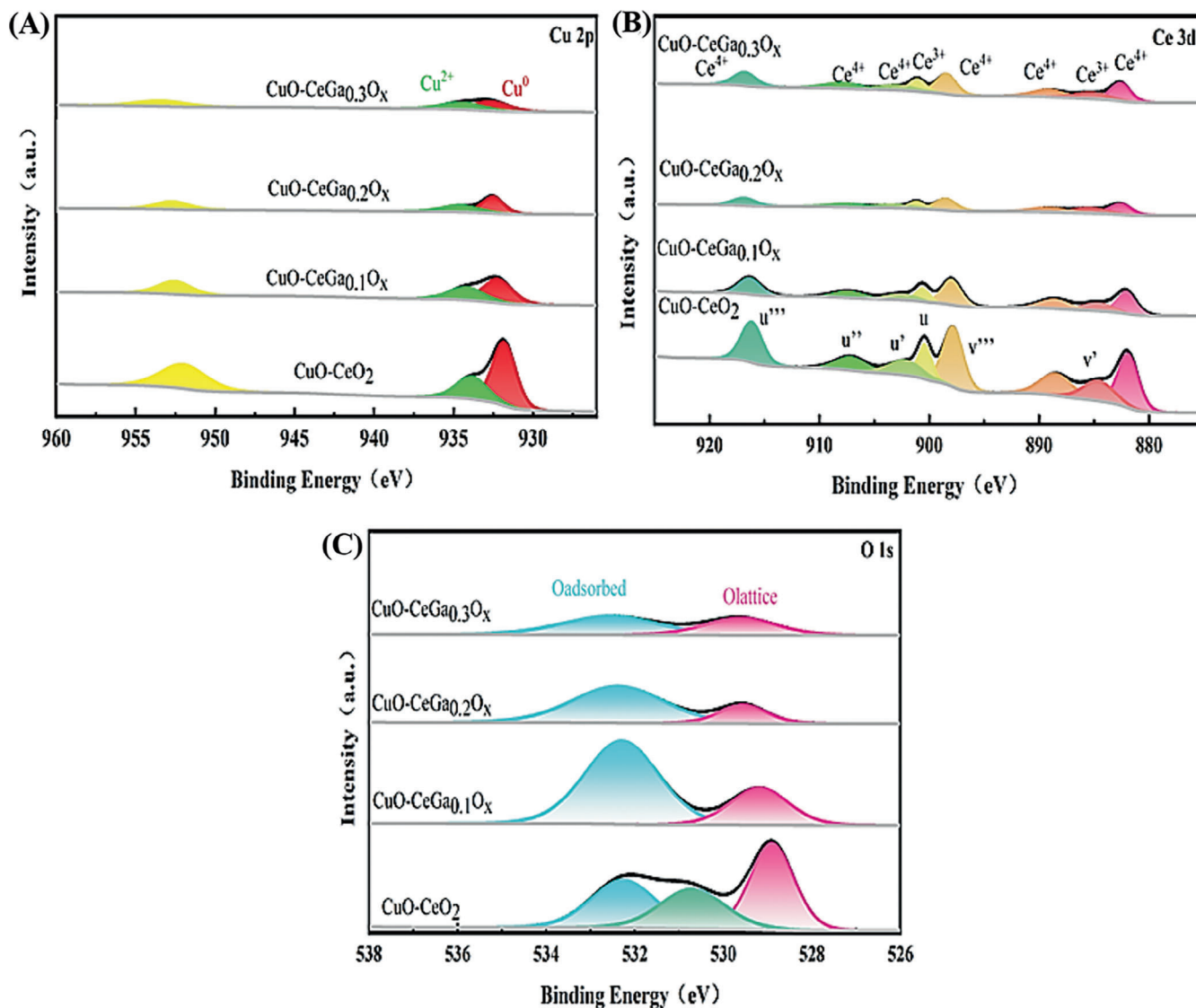


FIGURE 6 X-ray photoelectron spectroscopy (XPS) spectra of CuO-CeGa_yO_x ($y = 0, 0.1, 0.2, 0.3$) catalysts after hydrogen reduction: (A) Cu 2p, (B) Ce 3d, and (C) O 1s.

Catalysts	Cu ⁰ / (Cu ⁰ + Cu ²⁺) (%)	Ce ³⁺ / (Ce ³⁺ + Ce ⁴⁺) (%)	Percentage of chemisorbed oxygen (%)
CuO-CeO ₂	69.36	18.68	59.94
CuO-CeGa _{0.1} O _x	64.11	19.04	74.00
CuO-CeGa _{0.2} O _x	73.41	21.00	79.13
CuO-CeGa _{0.3} O _x	57.51	19.15	59.10

TABLE 2 X-ray photoelectron spectroscopy (XPS) data of CuO-CeGa_yO_x ($y = 0, 0.1, 0.2, 0.3$) catalysts after hydrogen reduction.

4 | EVALUATION OF CuO-CeGa_yO_x CATALYST ACTIVITY

Figure 7 summarizes the CO₂ conversion, methanol selectivity, CO selectivity, GHSV and STY of CuO-CeGa_yO_x ($y = 0, 0.1, 0.2, 0.15, 0.3$) catalysts under

conditions of 220–300°C, 12000 mL · g⁻¹ h⁻¹, and 5.0 MPa. Additionally, almost no CH₄ production was detected during the reaction. Figure 6A depicts the influence of temperature variation on CO₂ conversion for CuO-CeGa_yO_x catalysts. At 220°C, the CO₂ conversion rates of CuO-CeO₂, CuO-CeGa_{0.1}O_x, CuO-CeGa_{0.2}O_x, and

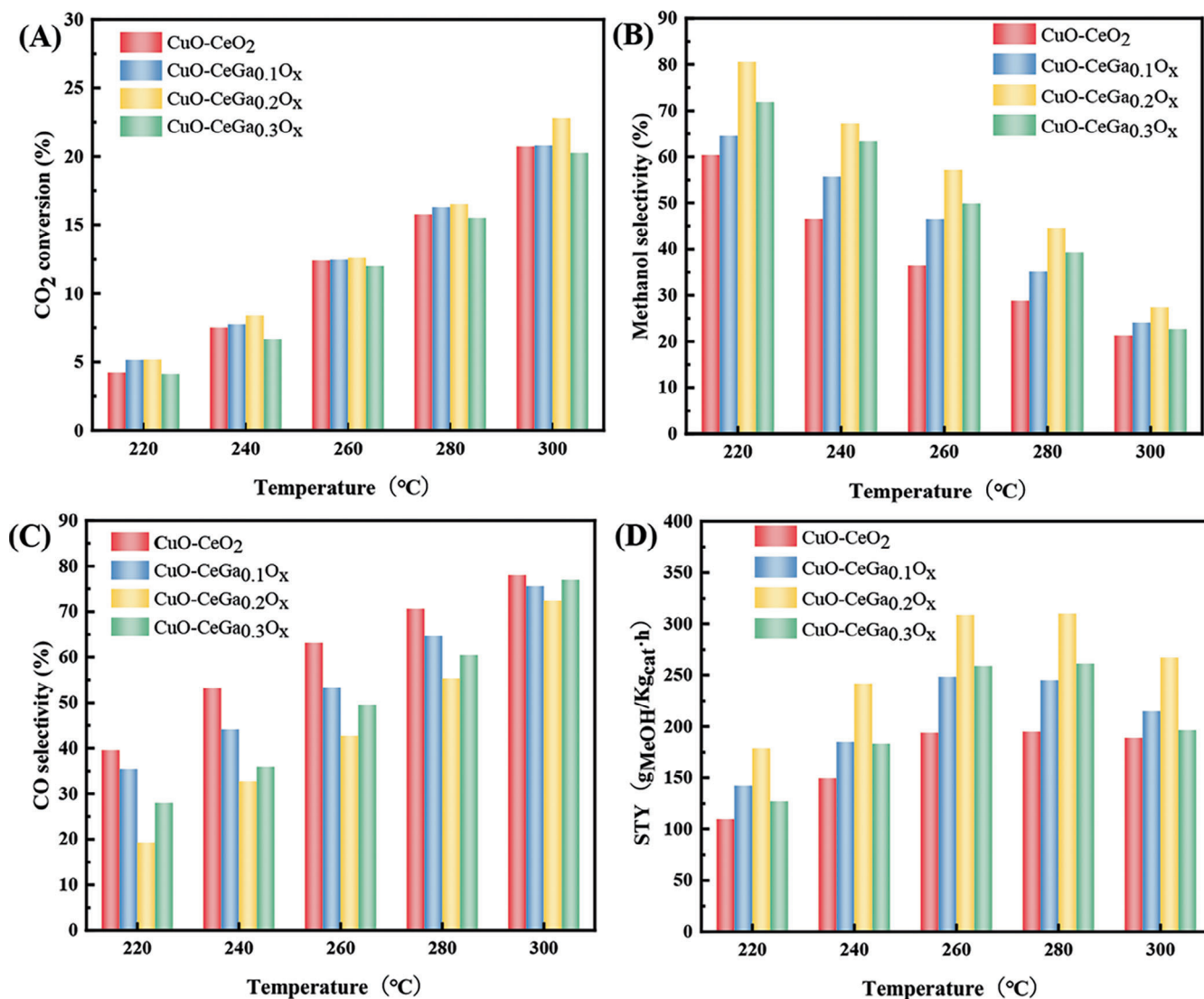


FIGURE 7 The catalytic performance of CuO-CeGa_yO_x (y = 0, 0.1, 0.2, 0.3) catalysts: (A) CO₂ conversion; (B) CH₃OH selectivity; (C) CO selectivity; and (D) space-time yield (STY).

CuO-CeGa_{0.3}O_x catalysts were 4.24%, 5.14%, 5.17%, and 4.13%, respectively. When the reaction temperature increased to 300 °C, the CO₂ conversion rates rose to 20.74%, 20.81%, 22.79%, and 20.25%, respectively. For all samples, the CO₂ conversion rate increased with temperature due to the thermodynamic inertia of CO₂ molecules, which became more easily activated at higher temperatures. Furthermore, a volcanic trend was observed in the CO₂ conversion rates of CuO/Ga_yCeO_x samples as the amount of Ga introduced increased. Notably, the CuO/Ga_{0.2}CeO_x sample exhibited superior CO₂ conversion rates compared to other samples at various reaction temperatures, ranging from 5.17%, 8.39%, 12.61%, 16.51%, and 22.79% within the temperature range of 220–300 °C. This is attributed to the strong interaction between Cu and GaCeO_x solid solution, which promotes the formation of oxygen vacancies and moderately strong

alkaline sites in the CuO/Ga_{0.2}CeO_x sample, enhancing its ability to adsorb and activate CO₂, thereby exhibiting excellent catalytic performance.

The selectivity of the primary product methanol and the main by-product CO over CuO/Ga_yCeO_x catalysts is shown in Figure 7B,C, respectively. At a reaction temperature of 220 °C, the methanol selectivity of CuO-CeO₂, CuO-CeGa_{0.1}O_x, CuO-CeGa_{0.2}O_x, and CuO-CeGa_{0.3}O_x catalysts were 60.38%, 64.56%, 80.64%, and 71.83%, respectively. When the reaction temperature increased to 300 °C, the methanol selectivity decreased to 21.28%, 24.1%, 27.34%, and 22.63%, respectively. The methanol selectivity of CuO-CeGa_yO_x catalysts is negatively correlated with the reaction temperature. This is because the methanol synthesis reaction is exothermic, while the RWGS reaction is endothermic. Therefore, as the temperature increases, the reaction favours the formation

of CO over methanol. Simultaneously, the methanol selectivity on CuO/Ga_yCeO_x samples exhibited a volcanic trend as the amount of Ga introduced increased at various reaction temperatures. Among them, the methanol selectivity of the CuO-CeGa_{0.2}O_x sample was superior to other samples at different reaction temperatures, ranging from 80.64%, 67.21%, 57.15%, 44.53%, and 27.34% within the temperature range of 220–300°C. The CO selectivity of the CuO-CeGa_{0.2}O_x sample was lower than other samples at different reaction temperatures, ranging from 19.30%, 32.70%, 42.75%, 55.32%, and 72.45% within the temperature range of 220–300°C. The relatively high number of Cu⁰ species in the CuO-CeGa_{0.2}O_x sample provides sufficient active H* species for the catalytic reaction, facilitating the conversion of CO₂ to methanol rather than CO. Additionally, moderately strong alkaline sites are more conducive to methanol synthesis, which explains the lower methanol selectivity on the CuO/CeO₂ catalyst.

Based on the experimental data of CO₂ conversion and methanol selectivity, the functional relationship between STY_{MeOH} and reaction temperature can also be derived (Figure 7D). At a reaction temperature of 260°C, the STY_{MeOH} of CuO-CeO₂, CuO-CeGa_{0.1}O_x, CuO-CeGa_{0.2}O_x, and CuO-CeGa_{0.3}O_x catalysts were 194.02 g_{MeOH} Kg_{cat}⁻¹ h⁻¹, 248.24 g_{MeOH} Kg_{cat}⁻¹ h⁻¹, 308.85 g_{MeOH} Kg_{cat}⁻¹ h⁻¹, and 258.91 g_{MeOH} Kg_{cat}⁻¹ h⁻¹, respectively. From Table S1, it can be seen that the CuO-CeGa_yO_x catalyst has excellent STY compared to the same type of CO₂ hydrogenation to methanol catalyst. Ga has a significant impact on the performance of the catalysts, with the STY_{MeOH} exhibiting a volcanic trend as the Ga content increases. Through comparison, the catalytic performance of CuO-CeGa_yO_x catalysts was higher than that of the CuO-CeO₂ catalyst. The CuO-CeGa_{0.2}O_x

catalyst, due to its abundant oxygen vacancies and highly dispersed Cu⁰ species, can effectively improve the adsorption performance of CO₂ and promote the dissociation of H₂, ultimately resulting in the best catalytic performance among the catalysts.

Reaction pressure is an important factor affecting the reaction effect of CO₂ hydrogenation to methanol, and Figure 8A shows the CO₂ conversion, methanol selectivity, and methanol spatial and temporal yields of CuO-CeGa_{0.2}O_x catalysts at different reaction pressures at a reaction temperature of 260°C and a reaction GHSV of 12,000 mL · g⁻¹ h⁻¹. As can be seen from the figure, the CO₂ conversion, methanol selectivity, and STY of methanol of the catalysts increased significantly with the increase of reaction pressure; when the reaction pressure was 2 MPa, the CO₂ conversion of the catalysts was 8.11% and the methanol selectivity was 35.1%, and when the reaction pressure was 5 MPa, the CO₂ conversion of the catalysts reached 12.61%, the methanol selectivity reached 57.15%, and the STY increased by 2.55 times. This is due to the fact that the reaction of CO₂ hydrogenation to methanol is a reaction of molecular number reduction, and the high pressure helps the reaction to proceed positively, which has less effect on the RWGS reaction, thus improving the methanol selectivity of the catalyst. However, too high pressure can lead to a significant increase in production cost, so it is necessary to choose a suitable reaction pressure of 5 MPa according to the actual situation.

Figure 8B shows the CO₂ conversion, methanol selectivity and methanol STY of the CuO-CeGa_{0.2}O_x catalysts at a reaction temperature of 260°C, a reaction pressure of 5 MPa and different reaction GHSV. As can be seen from the figure, the CO₂ conversion decreases with the increase of reaction airspeed, which is since the contact

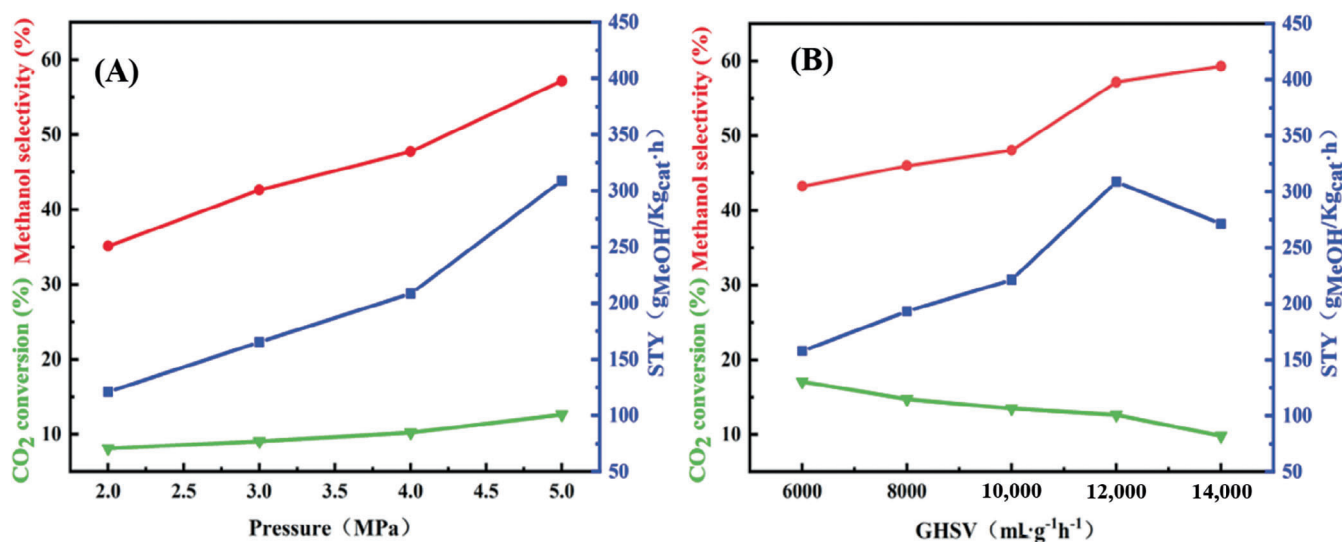


FIGURE 8 The catalytic performance of CuO-CeGa_{0.2}O_x under (A) different pressures and (B) gas hourly space velocity (GHSV).

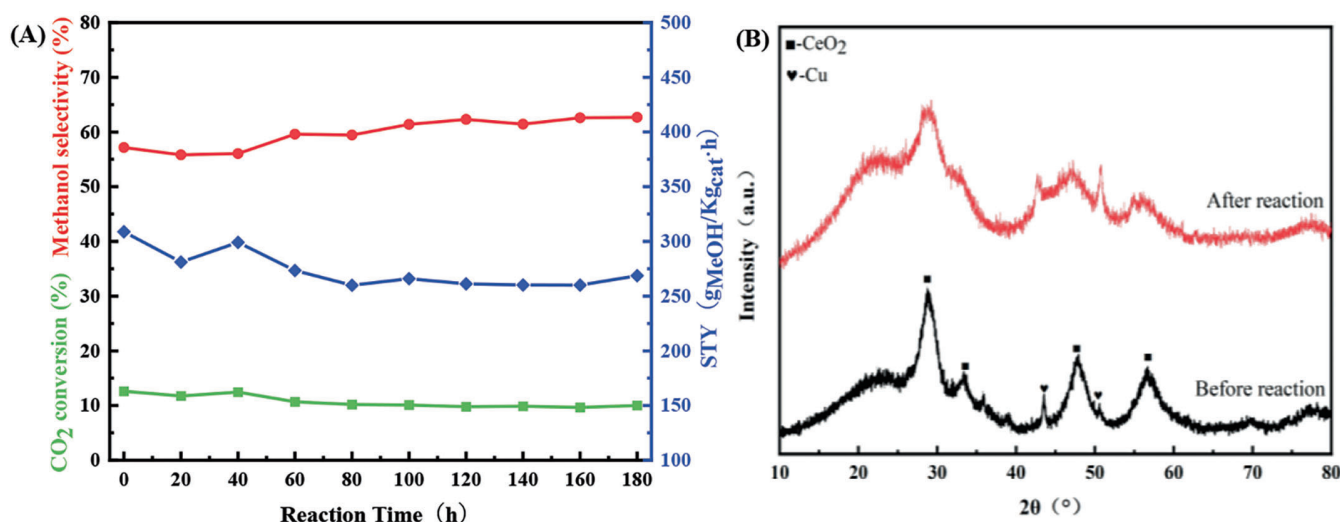


FIGURE 9 (A) CuO-CeGa_{0.2}O_x catalyst stability test; (B) X-ray diffraction (XRD) patterns of CuO-CeGa_{0.2}O_x catalyst after reduction and reaction.

time between the feed gas and the catalyst becomes shorter with the increase of reaction GHSV, which makes the feed gas unable to participate in the reaction sufficiently. The methanol selectivity increases with the increase of reaction GHSV, which indicates that the lower GHSV will make the contact time between the feed gas and the catalyst longer, thus the side reaction increases and reduces the methanol selectivity. When the reaction GHSV was 12,000 mL · g⁻¹ h⁻¹, the highest STY of CuO-CeGa_{0.2}O_x catalyst was 308.85 g_{MeOH} Kgcat⁻¹ h⁻¹, which was higher than those of the other GHSV, indicating that the optimum GHSV of CuO-CeGa_{0.2}O_x catalyst was 12,000 mL · g⁻¹ h⁻¹.

Figure 9A presents the stability test of the CuO-CeGa_{0.2}O_x catalyst ($T = 260^{\circ}\text{C}$, $p = 5\text{ MPa}$, $\text{GHSV} = 12,000\text{ mL} \cdot \text{g}^{-1}\text{ h}^{-1}$). The catalyst consistently maintains a stable performance over 180 h. With increasing reaction time, the CO₂ conversion rate remains within the range of 9.3%–12.6%, the methanol selectivity remains within 53%–62%, and the STY of methanol remains at 260–308 g_{MeOH} Kgcat⁻¹ h⁻¹, without showing a significant downward trend. Furthermore, Figure 9B displays XRD analysis of the catalyst before and after the reaction revealed no structural changes after long-term cycling, indicating that the CuO-CeGa_{0.2}O_x catalyst maintains good stability over 180 h of reaction time. This demonstrates that CuO-CeGa_{0.2}O_x has good potential for industrial applications.

5 | CONCLUSIONS

The incorporation of Ga³⁺ into CeO₂ lattice forms CeGaO_x solid solutions, which strengthen MSI by

generating Ce³⁺-induced oxygen vacancies and optimizing Cu⁰ dispersion. This dual effect enhances methanol selectivity. The CuO-CeGa_{0.2}O_x catalyst achieves a superior STY of 308.8 g_{MeOH} Kgcat⁻¹ h⁻¹ with 180 h stability, demonstrating scalability potential. This work establishes Ga-doped CeO₂ as a paradigm for engineering MSI in CO₂ hydrogenation catalysts, bridging fundamental insights with scalable solutions for carbon neutrality.

AUTHOR CONTRIBUTIONS

Tuo Guo: Conceptualization; investigation; writing – original draft; methodology; validation; visualization; writing – review and editing; formal analysis; data curation; software. **Wenwen Liu:** Investigation; visualization; validation; formal analysis; writing – review and editing; software. **Panpan Yang:** Conceptualization; investigation; writing – original draft; writing – review and editing; validation. **Qingjie Guo:** Conceptualization; methodology; supervision; resources; project administration; software; writing – review and editing; funding acquisition. **Pei Sean Goh:** Writing – review and editing; resources; formal analysis.

ACKNOWLEDGEMENTS

This work was supported by the National Foreign Experts Program (H20240298) and the Natural Science Foundation Project of Ningxia (2022AAC01001).

DATA AVAILABILITY STATEMENT

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

ORCID

Qingjie Guo  <https://orcid.org/0000-0001-6806-2089>

REFERENCES

- [1] X. Zhu, H. Zong, C. J. V. Perez, H. Miao, W. Sun, Z. Yuan, S. Wang, G. Zeng, H. Xu, Z. Jiang, G. A. Ozin, *Angew. Chem., Int. Ed.* **2023**, 62, e202218694.
- [2] C. Zuo, Q. Su, Z. Y. Jiang, *Molecules* **2023**, 28, 3982.
- [3] T. Guo, A. Cui, Y. Chen, M. Wu, Q. Guo, *J. Energy Inst.* **2025**, 118, 101947.
- [4] Y. Yuan, D. Zhai, J. Zhang, J. Ma, T. Guo, Y. He, Q. Guo, *Chem. Eng. J.* **2024**, 493, 152504.
- [5] M. Dai, T. Guo, X. Hu, J. Ma, Q. Guo, *Int. J. Hydrogen Energy* **2024**, 80, 298.
- [6] A. X. Cui, M. Wu, T. Guo, X. N. Sun, Y. L. Chen, Q. J. Guo, *New J. Chem.* **2024**, 48, 12616.
- [7] S. J. Xia, J. T. Gong, J. Yin, Z. Y. Zhao, F. Y. Tang, X. P. Guo, P. L. Liu, *J. Energy Inst.* **2023**, 109, 101302.
- [8] A. Boretti, *Int. J. Hydrogen Energy* **2013**, 38, 1806.
- [9] P. S. Murthy, W. B. Liang, Y. J. Jiang, J. Huang, *Energy Fuels* **2021**, 35, 8558.
- [10] J. Li, Q. Guo, X. Zhao, Y. K. Hu, S. Z. Zhang, Y. Zhao, S. Z. Li, *Mol. Catal.* **2023**, 549, 113494.
- [11] T. Q. Qi, Y. M. Zhao, S. Y. Chen, W. Z. Li, X. W. Guo, Y. C. Zhang, C. S. Song, *Mol. Catal.* **2021**, 514, 111870.
- [12] W. W. Wang, Z. P. Qu, L. X. Song, Q. Fu, *J. Energy Chem.* **2020**, 40, 22.
- [13] J. D. Zhu, Y. Q. Su, J. C. Chai, V. Muravev, N. Kosinov, E. J. M. Hensen, *ACS Catal.* **2020**, 10, 11532.
- [14] Y. Yan, R. J. Wong, Z. R. Ma, F. Donat, S. B. Xi, S. Saqline, Q. W. H. Fan, Y. H. Du, A. Borgna, Q. He, C. R. Müller, W. Chen, A. A. Lapkin, W. Liu, *Appl. Catal., B* **2022**, 306, 121098.
- [15] T. Guo, L. Wang, D. Zhai, Y. Yuan, Q. Guo, *ChemCatChem* **2025**, 2025, e202500103.
- [16] W. W. Wang, Z. P. Qu, L. X. Song, Q. Fu, *J. Energy Chem.* **2020**, 47, 18.
- [17] W. W. Wang, X. Y. Zhang, M. Guo, J. A. Li, C. Peng, *Front. Chem. Sci. Eng.* **2022**, 16, 950.
- [18] M. D. Nie, T. Guo, F. Y. Qiang, M. Wu, Y. Z. Liu, Q. J. Guo, Y. R. He, *React. Chem. Eng.* **2023**, 8, 1383.
- [19] H. Dai, A. H. Zhang, S. Q. Xiong, X. Xiao, C. J. Zhou, Y. Pan, *ChemCatChem* **2022**, 14, e202200049.
- [20] J. Vecchietti, P. Lustemberg, E. L. Fornero, M. Calatayud, S. E. Collins, S. Mohr, M. V. Ganduglia-Pirovano, J. Libuda, A. L. Bonivardi, *Appl. Catal., B* **2020**, 277, 119103.
- [21] J. Zuo, W. Na, P. Zhang, X. Yang, J. Wen, M. Zheng, H. Wang, *Mol. Catal.* **2022**, 526, 112357.
- [22] M. Behrens, I. Kasatkin, S. Köhl, G. Weinberg, *Chem. Mater.* **2010**, 22, 386.
- [23] M. Nie, A. Cui, M. Wu, T. Guo, Q. Guo, *J. CO₂ Util.* **2023**, 75, 102579.
- [24] N. Pasupulety, A. A. Al-Zahrani, M. A. Daous, S. Podila, H. Driss, *Arabian J. Chem.* **2021**, 14, 102951.
- [25] B. S. Xaba, A. S. Mahomed, H. B. Friedrich, *J. Environ. Chem. Eng.* **2021**, 9, 104834.
- [26] L. X. Song, H. Wang, S. Wang, Z. P. Qu, *Appl. Catal., B* **2023**, 322, 122137.
- [27] W. W. Wang, Z. P. Qu, L. X. Song, Q. Fu, *J. Catal.* **2020**, 382, 129.
- [28] S. Z. Li, L. M. Guo, T. Ishihara, *Catal. Today* **2020**, 339, 352.
- [29] V. D. B. C. Dasireddy, B. Likozar, *Renewable Energy* **2019**, 140, 452.
- [30] P. Gao, F. Li, H. Zhan, N. Zhao, F. Xiao, W. Wei, L. Zhong, Y. Sun, *Catal. Commun.* **2014**, 50, 78.
- [31] X. Wang, M. H. Alabsi, P. Zheng, J. Mei, A. Ramirez, A. Duan, C. Xu, K.-W. Huang, *J. Colloid Interface Sci.* **2022**, 611, 739.
- [32] K. Sun, Z. Fan, J. Ye, J. Yan, Q. Ge, Y. Li, W. He, W. Yang, C.-j. Liu, *J. CO₂ Util.* **2015**, 12, 1.

SUPPORTING INFORMATION

Additional supporting information can be found online in the Supporting Information section at the end of this article.

How to cite this article: T. Guo, W. Liu, P. Yang, Q. Guo, P. S. Goh, *Can. J. Chem. Eng.* **2025**, 1.
<https://doi.org/10.1002/cjce.25721>