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Effect of Ce and Zn on Cu-Based Mesoporous Carbon Catalyst for Methanol Steam Reforming

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Abstract

Hydrogen is a clean renewable energy with potential for future environmental sustainability. The main challenge in hydrogen production via methanol steam reforming (MSR) is carbon monoxide (CO) formation that deactivates the catalyst. In this study, the effect of zinc (Zn) and cerium (Ce) on copper–mesoporous carbon (MC)-catalyst (Cu–MC) for MSR was investigated. The highest surface area (380.5 m^2/g), observed for the Cu–MC prepared by one-pot (OP), decreased after incorporation of Ce and Zn. The temperature programmed reduction (H₂-TPR) studies showed a decrease in the reduction temperature of CuO. The metal oxides were well distributed over the MC support based on scanning electron microscopy (SEM) and transmission electron microscopy (TEM) studies. The MSR studies yielded methanol conversion of 65 and 68% for Ce-loaded Cu–MC prepared by OP and wet-impregnation (WI) methods at 300 °C and 250 °C, respectively. Addition of Zn to Cu–MC decreased methanol conversion, significantly, to 46%, at 300 °C. Both catalysts showed higher hydrogen selectivity, > 90%, with a lower CO selectivity for the Zn–Cu–MC catalyst. The Ce–Cu–MC (WI) catalyst showed good stability for 42 h with high H₂ selectivity, > 90%, and methanol conversion of 40% at 250 °C.

Graphical Abstract



Keywords Steam reforming \cdot Hydrogen \cdot Mesoporous carbon \cdot Cu–Zn \cdot Cu–Ce catalyst

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1 Introduction

Combustion of fossil fuels releases greenhouse gases like carbon dioxide (CO_2), carbon monoxide (CO), and nitrogen oxides (NOx) which have been polluting the atmosphere.

These gases can trap heat in the atmosphere, making them significant contributors to global warming and climate change [1]. In recent years, greenhouse gas emission has increased dramatically due to the extensive use of fossil fuels. This problem triggered many researchers to develop alternative fuels as energy resources. Hydrogen is considered an important candidate which has the highest energy density (143 MJ/kg) compared to any other known fuel. More significantly, the combustion of hydrogen for energy is a carbon-free process that produces water only as the byproduct; it is indeed a promising and viable route to reduce the greenhouse gases that cause global warming [2].

Hydrogen is a significant feedstock in industrial applications including hydrocracking, desulfurization processes, ammonia synthesis, Fischer-Tropsch synthesis, fertilizer for agriculture, and fuel cells [3–5]. More specifically, fuel cells have been used for generating electricity by electrochemical reactions. It has very low emissions of pollutants and is highly efficient compared to fossil fuels [6]. Hydrogen is believed to be a valuable clean alternative energy source for fuel cell applications [7]. Hydrogen-powered proton exchange membrane fuel cells (PEMFC) provide an effective and more economical option to generate energy [8]. Currently, hydrogen used for fuel cells is generally produced by reforming processes. The major challenge is the production of undesired carbon monoxide that reduces the lifetime of the platinum electrode [9]. So, researchers are trying to develop catalysts that can reduce the amount of carbon monoxide in the reforming process. Another challenge for fuel cell applications is the transportation, storage, and safety concerns of hydrogen due to its unique properties. To overcome these problems, it is necessary to look for new technologies for on-site hydrogen production from different energy resources [10].

Several methods such as water electrolysis, hydrocarbon reforming, and photocatalysis have been studied to produce hydrogen over the years [11]. As mentioned above, hydrocarbon reforming has been extensively used for hydrogen production from renewable and non-renewable resources. The reforming process is known as catalytic reforming, which is the chemical process that breaks down the hydrocarbon and alcohol to produce H_2 [11]. Different types of reforming processes such as steam reforming, partial oxidation, dry reforming, and auto-thermal reforming are used to produce H_2 [12]. Steam reforming produces the maximum amount of H₂ compared to all other reforming processes. Steam reforming of alcohols such as methanol [13–15], ethanol [16, 17], and glycerol [18-20] has been the major focus of steam reforming in recent years. The advantage of an alcohol is that it can react with water vapor and produce enough hydrogen gas at lower temperature [21]. Methanol steam reforming (MSR) is highly favorable due to its much lower conversion temperature and optimum for its high hydrogen-to-carbon ratio. In addition, the absence of a C–C bond in methanol makes it viable for commercial hydrogen production via steam reforming in the temperature range of 200-300 °C [11].

Steam reforming reactions, shown below, take place in three different steps. The first reaction shown in Eq. (1) is the primary reaction. Methanol reacts with the water, producing carbon dioxide (CO_2) and three moles of hydrogen. This reaction is endothermic requiring energy to initiate the reaction [22]. During the main reaction (MSR), two side reactions commonly occur. In Eq. (2), decomposition of methanol produces one mole of carbon monoxide (CO) and two moles of hydrogen. The carbon monoxide produced then undergoes a water-gas shift reaction shown in Eq. (3) [23]. In the water-gas shift reaction, carbon monoxide reacts with water and produces one mole of carbon dioxide and hydrogen. The by-product of the MSR reaction is carbon monoxide; if the concentration of CO increases, it can poison the catalyst and deactivate its function. The water-gas reaction is necessary to convert the undesired CO into carbon dioxide so that the catalyst can remain active. The active catalyst produces hydrogen while keeping a minimal amount of carbon monoxide in the steam reforming process [22, 24].

Main reaction:

Methanol steam reforming reaction:

$$CH_3OH + H_2O \rightarrow CO_2 + 3H_2\Delta H = 49.5 \text{ kJ/mol}$$
(1)

Side reactions:

Decomposition of Methanol:

$$CH_3OH \rightarrow CO + 2H_2\Delta H = 90.6 \text{ kJ/mol}$$
(2)

Water - gas shift reaction: $CO + H_2O \rightarrow CO_2 + H_2\Delta H = -41.2 \text{ kJ/mol}$ (3)

Noble metals such as Rh, Ir, Pt, Ru, and Pd, have shown high activity in steam reforming of alcohols [25], and Rh is regarded as one of the most active among the noble metals [26]. However, the high cost of noble metals hinders them from scale-up and commercialization [27]. In contrast, copper, as a low-cost metal, is highly active in methanolreforming [25]. However, copper-containing catalysts suffer from deactivation due to the changes in the oxidation state, sintering, or coke deposition on the catalyst [11]. Various promoters are usually added to increase the stability of the copper-based catalyst and the hydrogen yield in MSR [27]. For example, the addition of Ni to the copper monometallic catalyst significantly increases its resistance to deactivation [28].

In addition to metals, the use of support with high surface areas plays an important role in improving catalytic performance. The use of copper catalyst on CeO₂ support, reported by Liu et al., suggests that the cerium (IV) oxide favors the dispersion of copper particles and enhances the stability of Cu, resulting in enhanced performance in MSR [29]. Zinc oxide, as the catalyst support, has also shown enhanced CO_2 selectivity in MSR [30]. This is due to its ability to promote low-temperature water-gas shift reactions. In this paper, we have used two inexpensive metals, i.e., Ce and Zn, as the promoters in the copper-based catalysts for MSR using mesoporous support such as mesoporous carbon (MC). Mesoporous materials have been widely used as catalysts due to their ordered pore structure, large pore volume, and chemical inertness. More specifically, mesoporous carbon (MC) has been used for ethanol steam reforming [31]. However, it was not used for MSR, and suppression of CO has not been investigated with effective promoters. Consideration of the advantages of mesoporous carbon as catalyst support with high surface area for metal loading, high pore volume for mass transfer, and proven improvement in ethanol steam reforming at a lower temperature [31], prompted us to investigate it as the support for MSR in the presence of Cu-catalyst and promoters. In other studies, the mesoporous carbon showed better results at lower temperatures, making it ideal for methanol steam reforming [31]. Mesoporous carbon has physicochemical properties, such as electron conductivity and ideal hydrothermal stability [31], essential for development of robust catalysts for fuel cell applications. Extensive characterization of the catalysts containing CeO₂ and ZnO as promoters and the effect of these metals on their performance in MSR are reported in this paper.

2 Experimental

2.1 Materials and Methods

Copper(II) chloride dihydrate (CuCl₂ 2H₂O), cerium(III) nitrate hexahydrate (Ce(NO₃)₃ · 6H₂O), and zinc nitrate hexahydrate (Zn(NO₃)₂ · 6H₂O) salts, resorcinol and formaldehyde were used as copper, zinc, cerium and carbon resources. Pluronic F127 was used as a template and sodium hydroxide pellets (NaOH) were used to control the pH of the solution. Absolute ethanol was used as the solvent. All materials were purchased from Sigma-Aldrich.

2.2 Catalyst Preparation

2.2.1 One-Pot Synthesis of Cu on MC, CuCe on MC and CuZn on MC Catalysts

Copper (Cu) on MC was synthesized by the one-pot hydrothermal method as described by Amini et al. [31]. In a beaker, 1.3 g of resorcinol was dissolved in 20.8 g of pure ethanol. Then, 0.04 g of sodium hydroxide was dissolved in the as-prepared solution, and 2.9 g of formaldehyde was added. Then the solution was mixed for 30 min until the solution was homogeneous and transparent. During this time, in another beaker, 2.6 g of the F127 template was dissolved in 15.6 g of ethanol at 30 °C, and then 0.3 g of copper chloride and 0.3 g of cerium nitrate were added and dissolved into this solution. After the first solution was completely clear, it was added dropwise to the second solution containing the metal precursor. After titration, the solution was stirred at 25 °C for 2 h. To evaporate the ethanol, the solution was kept at 25 °C for 24 h and then heated in the oven at 110 °C for 24 h. Finally, the catalyst was carbonized in an Ar atmosphere at 700 °C for 2 h with a heating rate of 1.5 °C/min. Cu, Ce and Zn-based MC materials were prepared following a similar procedure. The catalysts synthesized by one-pot method are denoted as Cu on MC (OP), CuCe on MC (OP), and CuZn on MC (OP).

2.2.2 Wet-Impregnation Synthesis of CuCe on MC Catalyst

CuCe on MC was synthesized by the wet-impregnation or impregnation method. First, mesoporous carbon (MC) was prepared by the procedure described above. Then, the proportional amount of CuCl₂ and Ce(NO₃)₃ salt solutions were prepared and impregnated over the MC support. After that, the catalyst was dried in a hot air oven at 110 °C for 6 h and finally, it was calcined in air at 550 °C for 4 h. The catalyst prepared in this method is denoted as CuCe on MC (IMP).

2.3 Catalyst Characterization

The N₂ adsorption-desorption isotherms of all the different catalysts were measured by the surface area analyzer (Model: 3Flex, Make: Micromeritics, USA) at the constant temperature of -196 °C (liquid N₂) The N₂ adsorption–desorption isotherm was used with the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) method to calculate the surface area and pore size distribution. Temperature-programmed reduction (TPR) analysis was carried out using a chemisorption analyzer (Mode: 3Flex, Make: Micromeritics, USA). In the chemisorption tube, 0.05 g of sample material was weighed and placed into the tube. The top of the chemisorption tube was covered by a layer of quartz wool following the quartz filter cap where the sample was placed in the port of the instrument. The sample was then placed under a 10% H₂/Ar (1:9wt %) flow of 50 ml/min with a ramp rate of 10 °C/min from room temperature to 700 °C. This will help determine the reducibility of the metal oxides. The X-Ray diffraction (XRD) was carried out using a powder X-Ray diffractometer (Model: Bruker AXS) with a detection limit in the range of 10° - 80° with a step interval of 0.02° using a Cu Kα1 radiation (wavelength, 1.5406 Å). The XRD peaks were used to classify the metals, the morphology, and the oxidation states of metal in the catalysts. The microscopic images of the catalysts were obtained using the ZEISS Auriga focused ion beam scanning electron microscope (FIBSEM). The images were used to determine the morphology, topology, and particle size of the catalysts. The transmission electron microscopy (TEM) was carried out using Thermo Fischer Talos (Model: F200X). The field emission system was operated at 200 kV. The oxidation states and bonding energy of all catalysts were determined by X-ray photoelectron spectroscopy (Model: Escalab Xi+-, Make: Thermo Scientific, West Sussex, UK). The FTIR spectra were recorded using Shimadzu IR Prestige-21 Fourier transform infrared (FTIR) 8300 spectrometer equipped with mercurycadmium-telluride (MCT) detector. Thermogravimetry and Differential scanning Calorimetry (TGA-DSC) (Model: TA instruments, New Castle, DE, USA) were used to observe the decomposition temperature of the polymer templates and the heat flow of the reactions.

2.4 Catalyst Activity Test

All catalysts were reduced first ex-situ in the presence of 10% H₂ in Ar at 550 °C for 5 h in the tubular muffle furnace [13]. The catalyst activity was tested in a packed bed stainless-steel tubular reactor (Tube ID:6.22 mm) [13]. The reduced catalyst was mixed with sand (white quartz, 50-70 mesh, supplier: Sigma-Aldrich) at a volume ratio of 2. Then the catalyst-sand mixture was loaded into the reactor and quartz wool was used on both ends of the reactor. Before the start of the methanol steam reforming reaction, the catalyst was activated further in situ by 10% H₂ in Ar at 350 °C for 2 h to ensure the reduced state of the catalyst. The reaction products and condensate were analyzed using Agilent 7890B GC equipped with TCD and FID detectors. The Eqs. (4)–(6)were used to calculate the methanol conversion and selectivity to H₂ and CO by examining the moles in the condensate and the moles of H₂, CO, and CO₂ in the product gas stream of MSR reaction [13].

$$X_{Methanol} = \frac{CH_3OH \text{ moles converted}}{CH_3OH \text{ moles fed}} \times 100\%$$
(4)

$$S_{CO} = \frac{CO \text{ moles in product}}{(CO_2 + CO + CH_4) \text{ moles in product}} \times 100\%$$
(5)

$$S_{H_2} = \frac{H_2 \text{ moles in product}}{RR \times (CO_2 + CO + CH_4) \text{ moles in product}} \times 100\%$$
(6)

The coefficient RR is the H_2/CO_2 reforming ratio which is equal to 3 for the MSR process.

3 Results and Discussion

3.1 Catalyst Characterization

3.1.1 N₂ Physisorption Analysis

The N₂ physisorption analysis was carried out to determine the textural properties of the catalysts. Table 1 presents the surface area, pore volume, and average pore diameter of the calcined catalysts. The mesoporous carbon has a surface area of 295.1 m²/g and a pore volume of 0.165 cm³/g. After the addition of copper, the surface area and the pore volume increased to 380.5 m²/g and 0.362 cm³/g, respectively. This may be due to the formation of Cu nanoparticles over the support surface, which helps to increase the number of pores over the mesoporous carbon support. So, the pore volume increased. The surface area increased due to the increase in pore volume. In contrast, incorporation of CeO₂ and ZnO filled the support pores and made them inaccessible for N₂ adsorption. The average pore diameter of all catalysts increased except for CuCe on MC (OP). This is because smaller pores are blocked first and help to increase the avg. pore diameter. The variation in average pore diameter has also been observed by Panpranot et al. [32].

All catalysts exhibit hysteresis loops in Fig. 1a, indicating the existence of the mesoporous structures. The CuZn on MC (OP) catalyst showed the lowest surface area and pore volume. It's not quite clear why the surface area increases after the addition of Cu to MC. However, a decrease in surface areas after the addition of Cu and Ce corresponds to the decline of the hysteresis loop width. Cu on MC (OP) catalyst exhibited a Type IV isotherm with an H₂-type hysteresis loop, which according to the IUPAC classification confirms the mesoporous structure with cage-like channels [33]. In the case of Cu on MC (OP) catalyst, the linear increase of N_2 uptake at low relative pressure (P/P_0 = 0-0.45), depicts the monolayer-multilayer adsorption on the pore wall followed by a stepwise N₂ uptake at a relative pressure (P/ $P_0 = 0.45 - 0.5$). This indicates a capillary condensation in the mesopores. Figure 1b shows the pore size distribution

 $\label{eq:constraint} \begin{array}{l} \textbf{Table 1} & \text{Surface area, pore diameter and pore volumes of different} \\ \textbf{Cu-MC-based catalysts} \end{array}$

Catalyst	Surface area (m ² /g)	Pore volume (cm ³ /g)	Avg. pore diameter (nm)
MC	295.1	0.165	2.24
Cu on MC (OP)	380.5	0.362	3.81
CuCe on MC (OP)	316.6	0.174	2.20
CuZn on MC (OP)	102.9	0.127	4.94
CuCe on MC (IMP)	199.3	0.139	2.8



Fig. 1 Nitrogen adsorption-desorption isotherms and the pore size distributions of the calcined (a, b) MC support and Cu-MC-based catalysts

of support and catalysts. The distribution profile of Cu on MC (OP) catalyst shifted to the right compared to other catalysts and the intensity of the profile increased, which showed higher pore volume. The distribution profile of other catalysts showed a lower intensity peak that corresponds to lower pore volume compared to Cu on MC (OP) [31].

3.1.2 Temperature Programmed Reduction (TPR)

H₂-TPR analysis was carried out to investigate the reduction behavior of the metal oxides in all catalysts. Cu-based catalysts are highly active in methanol steam reforming reaction due to lower reduction temperatures [34, 35]. TPR experimental parameters including the heating rate of the sample, flow rate, and composition (H₂ concentration) of the reducing gas affected the reduction temperature [36]. If these three parameters are fixed, then the particle size (20 nm as per SEM image) and metal-support interaction would play important roles in the reduction behavior of the samples [37]. Pure CuO particles were reduced at a higher temperature compared to supported CuO particles [37]. This means that metal-support interaction could facilitate CuO reduction. The bulk and supported CuO particles were reduced by nucleation or autocatalytic reduction processes [38]. In the case of the Cu on MC (OP) catalyst, one broad peak in the temperature range of 150-350 °C (Fig. 2) is due to the reduction of copper oxide (CuO \rightarrow Cu⁰) particles, which have poor interaction with mesoporous carbon support [37]. The overlapping reduction peaks are observed for CuCe on MC (OP) catalyst. Different peaks indicate the presence of more than one copper species in the catalyst and reduction occurrs in steps. More specifically, three overlapping peaks for this catalyst are observed: a low-temperature peak of low intensity corresponds to the reduction of copper ions strongly interacting with CeO2 and two peaks of higher intensity ascribed to the reduction of larger CuO particles less interacting with ceria [39, 40]. The TPR profile of the CuZn on MC (OP) catalyst is almost the same as Cu on MC (OP) catalyst. Only one reduction peak observed at 330 °C corresponds to CuO reduction. For CuCe on MC (IMP) catalyst, two reduction peaks are observed at 341 and 376 °C. The first peak at 341 °C is attributed to the reduction of CuO. The slightly higher reduction temperature (376 °C) for the impregnated catalyst corresponds to the reduction of CuO that interacts with CeO₂. The higher temperature peak at 500–650 °C possibility corresponds to the formation of methane, due to the reaction between the carbonaceous support and H₂ [31]. In addition, the strong interaction of cooper oxide with support provides the reduction of CuO at



Fig. 2 TPR profiles of: (a) Cu–MC, (b) CuCe–MC, (c) CuZn–MC, (d) CuCe–MC (IMP) catalysts

a higher temperature, which is overlapped by the methanation peak [31].

Table 2 shows the hydrogen consumption of all catalysts during the TPR analyses. The highest H_2 consumption is observed for CuCe on MC (OP) catalyst which reflects the presence of a maximum number of reducible species. For other catalysts, the same amount of H_2 is consumed. The lowest H_2 consumption is observed for the CuCe on MC (IMP) catalyst. This may be due to clogging of the pores of Cu on MC by CeO₂.

3.1.3 X-Ray Diffraction (XRD)

The XRD patterns of all catalysts are shown in Fig. 3. For catalysts prepared by a one-pot procedure, a broad peak is observed in the range of $2\theta = 15^{\circ} - 30^{\circ}$, indicating the structure of an amorphous support [31]. In all one-pot preparation of catalysts, three peaks at $2\theta = 43.12^{\circ}$ (111), 50.34° (200) and 74.02° (220) (JCPDS-04-0836) with cubic structure confirm the presence of Cu metal in MC support after carbonization. In the case of CuCe on MC (OP) catalyst, Ce metal is found at $2\theta = 28.52^{\circ}$ (101), 47.52° (105), 69.65° (108) and 76.65° (206) (JCPDS-89-2728) angle with a hexagonal structure after carbonization. In the case of the CuZn on MC (OP) catalyst, the Zn metal peak is observed at $2\theta = 34.31^{\circ}$ (112), 31.75° (110), 36.41° (201) and 45.45° (203) (JCPDS-01-1238) with a hexagonal structure after carbonization. In the case of CuCe on MC (IMP) catalyst, the CuO crystal phases are present at $2\theta = 31.53^{\circ}$ (110), 35.40° (111), 38.79° (200), 45.23° (112) and 61.26° (113) (JCPDS-89-2531) with monoclinic structure after calcination. CeO₂ is found at $2\theta = 28.52^{\circ}$ (111), 32.92° (200), 47.52° (220), 56.40° (311), 69.65° (400) and 76.65° (331) (JCPDS-81-0792) angle with a cubic structure for CuCe on MC (IMP) catalyst after calcination in presence of air. The peak intensity is reduced after the addition of Ce for the one-pot CuCe catalyst on MC support as Ce is distributed throughout the sample. In contrast, higher peak intensity is observed for CuCe on MC (IMP) catalysts. This suggests that the impregnation method facilitated the crystal growth during material preparation. In the impregnation method, the metals are distributed over the upper layer of the support of the catalyst,

Table 2 H₂ consumption by Cu–MC-based catalysts

Catalyst	H ₂ consump- tion (mmol/g)		
Cu on MC (OP)	0.266		
CuCe on MC (OP)	0.298		
CuZn on MC (OP)	0.255		
CuCe on MC (IMP)	0.095		



Fig. 3 XRD profiles of: (a) Cu–MC, (b) CuCe–MC, (c) CuZn–MC, (d) CuCe–MC (IMP) catalysts

this causes the intensity of the peak to increase compared to that prepared by the one-pot method [41].

Table 3 shows the average crystal size of all metal oxides. The average crystal size is calculated using the modified Scherrer equation [42]. The Cu metal crystal size for the Cu on MC (OP) catalyst is 16.92 nm. The Cu metal crystal size (14.65 nm) decreases slightly after the addition of Ce metal (19.92 nm) in the CuCe on MC (OP) catalyst. The smaller Cu metal crystal size indicates that the addition of Ce metal increases the interaction between Cu and Ce [43]. In the case of impregnated CuCe on MC (IMP) catalyst, the crystal sizes of CuO and CeO₂ are 27.56 and 16.96 nm respectively. The higher CuO crystal size of impregnated catalyst suggests a weak interaction between CuO and CeO₂. Wang et al. [44] showed that the larger size of CeO₂ has lower structural defects compared to small crystal size. The Cu metal crystal

 Table 3
 Crystal size calculation for different Cu–MC-based catalysts

Catalyst	Crystal Size (nm)			
	Cu CuO	Ce CeO ₂	Zn	
Cu on MC (OP)	16.92	_	_	
CuCe on MC (OP)	14.65	19.92	-	
CuZn on MC (OP)	21.42	_	20.16	
CuCe on MC (IMP)	- 27.56	- 16.96	-	

Using modified Scherrer equation [42]

size of the CuZn on MC (OP) catalyst is high compared to that of CuCe on MC (OP) catalyst.

3.1.4 Transmission Electron Microscopy (TEM)

TEM experiments were carried out to study the mesoporous carbon structure and distribution of metal particles over the support in the calcined catalysts as shown in Fig. 4. In all micrographs, mesopores are observed, which confirms the mesoporous structure of the carbon support, in agreement with N₂ physisorption analysis [31]. Similar kind of mesoporous structure of MC is obtained by Suliman et al. [45]. After the addition of metal particles, the mesoporous structure of MC does not change. The mesoporous structure is clearly visible in CuCe on MC (OP) catalyst. The TEM images showed a better distribution of metals in the support for one-pot hydrothermal synthesis compared to that obtained by the impregnation method. However, the structure changed in the case of wet-impregnated catalysts (Fig. 4e). Some rod-type particles are observed over the mesoporous carbon support. This different structure is formed possibly due to thermal exfoliation during calcination at higher temperature in presence of air for impregnated catalyst. As a result, the mesoporous carbon structure is distorted. Similar results were obtained by Ahmad et al. [46]. Nguyen and Tran showed that the mesoporous carbon catalyst is not stable in air at high temperature due to its organic structure (C–C chains) [47]. The TEM image of our impregnated catalyst is provided in the supplementary document (See Fig. S1). In the case of the CuZn on MC (OP) catalyst (Fig. 4d), the agglomeration of particles is observed over the carbon support, which might negatively affect the activity in MSR. CuCe on MC (OP) catalyst shown in Fig. 4c exhibits a good distribution of metal particles over the support. The pores of the support have been blocked by the metals, which tends to decrease the pore volume [31, 48]. It may also result in interfacial voids in the carbon matrix by the addition of metal particles. This result is in reasonable agreement with N₂ adsorption–desorption analysis.

3.1.5 Scanning Electron Microscopy (SEM)

Figure 5 shows the surface morphologies of MC and other catalysts. The SEM images show that the MC and MC-supported catalysts are agglomerated of small irregular particles [49]. In the case of the CuCe on MC (OP) catalyst, there are some tapered-shaped particles over the support (Fig. 5c). Rod-type particles are found for CuCe on MC (IMP) catalyst (Fig. 5e). This suggests that the preparation technique of the catalysts plays an important role to yield a different morphology of the catalyst. The bigger size of particles is observed in the case of CuZn on MC (OP) catalysts (Fig. 5d). These results are in reasonable agreement with the

TEM analysis. The average particle size of all the catalysts is 20.43 nm. The avg. particle size was measured by ImageJ software. The elemental mapping of all catalysts is done by SEM analysis (see Figs. S2 to S5).

3.1.6 FTIR Studies of Catalysts

The spectrum of FTIR helps to determine the functional groups within the catalyst. Figure 6 shows the FTIR spectra of the as-synthesized catalysts (MC–As, Cu–MC–As, CuCe–MC–As, and CuZn–MC–As). As the "As-synthesized catalyst" is obtained after drying, it contains F127 and other structure-directing agents. The presence of a broad peak at 3437 cm⁻¹ corresponds to the –OH groups [50, 51]. The –CH₂ stretching vibration is observed at 2877 cm⁻¹ due to the intermolecular interaction between resorcinol–formal-dehyde [52].

The 1608 cm⁻¹ peak can be assigned to the C=C (alkene) bond [53]. The skeletal C=C vibrations of the aromatic ring is observed at 1474 cm⁻¹ [54]. The –CH₂ wagging vibration is observed at 1360 cm⁻¹ and proves the presence of F127 in the sample [55]. The C–O–C asymmetrical axial deformation of the ether peak is observed at 1242 cm⁻¹ [54]. The peak at 1098 cm⁻¹ is assigned to C–O stretching [56]. The assigned peak at 944 cm⁻¹ corresponds to the CH₂ rocking or C–O–C stretching band of Pluronic F127 [57, 58]. These bands are not observed in the FTIR spectra of catalysts after calcination as they are removed in this process (see Fig. S6).

3.1.7 TGA–DSC Analysis of All Uncalcined Catalysts

TGA–DSC analyses of the samples are depicted in Fig. 7. In each thermogram, there are three weight losses observed for each one of the as-synthesized catalysts. The first weight loss below 150 °C corresponds to elimination of the moisture adsorbed on the surface of the catalyst [59]. The second weight loss between 150 and 400 °C is due to the decomposition of Pluronic F127 molecules from the as-synthesized catalyst for all one-pot catalysts [60, 61]. The weight loss between 400 to 1000 °C is due to carbonization of the polymeric material (Resorcinol and Formaldehyde) [62].

3.1.8 X-Ray Photoelectron Spectroscopy Analysis

The chemical oxidation states of all elements in the catalysts are determined using XPS analysis (Fig. 8). Figure 8a shows the binding energy of C1s for all calcined catalysts. The carbon in all the MC support, Cu–MC (OP) and CuCe–MC (IMP) catalysts show a narrow XPS spectrum which is centered at the binding energy of 283.95 eV. After the addition of Ce and Zn, the binding energies of both CuCe–MC and CuZn–MC (OP) decreased to 282.64 eV, indicating weaker interactions of Ce and Zn with the carbon support. The



Fig. 4 TEM micrographs of all catalysts: a MC; b Cu on MC (OP); c CuCe on MC (OP); d CuZn on MC (OP); e CuCe on MC (IMP)

slight variance in the C1s spectra of Ce- and Zn- modified catalysts with different methods suggests that both the metal species and the incorporation methods affect the interaction of metals with the support matrix [63, 64]. The comparison of the binding energy of Cu_{2p} between Cu–MC and

CuZn–MC is shown in Fig. 8b. The feature peaks of Cu–MC (OP) catalyst are observed at 961.80, 953.43, 941.68 and 933.21 eV [65, 66], respectively. After incorporation of Zn, the peaks shifted to 960.60, 952.04, 940.18 and 932.41 eV, respectively, exhibiting a decreased binding energy. The



Fig. 5 SEM images of all catalysts: a MC; b Cu on MC (OP); c CuCe on MC (OP); d CuZn on MC (OP); e CuCe on MC (IMP)

combination of Ce3d and Cu2p are displayed in Fig. 8c. CuCe–MC (OP) and CuCe–MC (IMP) both have the same binding energy observed for Cu–MC (OP), indicating the effects of Ce on the Cu-support interactions was limited. The peaks at 915.85, 898.87 and 882.39 eV of both catalysts were attributed to CeO_2 [67]. However, the intensity of the CuCe–MC prepared via one-pot is much weaker than that prepared via WI method. It is most likely due to the greater

density of Ce when impregnated on MC surface. Thus, the preparation method and the metal that is incorporated in the support play a major role in designing the catalyst because of the difference in interactions of the support with the metal or catalyst [68–70]. In Fig. 8d, Zn_{2p} binding energies observed at 1020.34 and 1043.16 eV in CuZn–MC (OP) confirm the presence of ZnO, which is in agreement with the XRD analysis [66, 71].



Fig. 6 FTIR analyses of all as-synthesized catalysts: (a) MC–As; (b) Cu on MC–As; (c) CuCe on MC–As; (d) CuZn on MC–As

3.2 Catalyst Activity Test

3.2.1 Effect of Temperature on Methanol Conversion

To study the effect of temperature on all catalysts' activity, the MSR reactions were carried out in the temperature range of 200 to 350 °C with fixed steam to methanol molar ratio of 3 and gas hourly space velocity (GHSV) of 2900 h^{-1} [13]. Our studies are similar to that of other researchers who studied methanol steam reforming in this temperature range with fixed reaction parameters [72, 73]. All the catalysts showed promising results for methanol conversion. For all one-pot synthesized catalysts, the highest methanol conversion was obtained at 300 °C, whereas in the case of impregnated catalysts, the highest conversion was observed at 250 °C. Therefore, it can be concluded that all catalysts worked well in the low-temperature regime, 250 to 300 °C. The highest methanol conversion was achieved at around 68% for the CuCe-MC (IMP) catalyst at 250 °C. This is comparable to the Cu catalysts supported on mesoporous silica (MCM-41) under the similar condition of 250 °C and 2838 h⁻¹ GHSV [13], indicating that mesoporous carbon is also an outstanding support for catalytic steam reforming reactions. The lower methanol conversion is observed in this temperature range due to the agglomeration of active sites of the catalysts [31]. A 65% conversion is obtained for CuCe-MC (OP) catalyst at 300 °C. So, further studies were carried out with these two catalysts at different temperatures (Fig. 9).

3.2.2 Effect of Temperature on Product Selectivity

Figure 10 shows the effect of temperature on the selectivity of product gases. For Cu–MC (OP), CuZn–MC (OP) and CuCe–MC (IMP) catalysts, over 95% H_2 selectivity

was observed in the temperature range of 200 to 350 °C. The H_2 selectivity decreased at a higher temperature for CuCe-MC (OP) catalyst. In the case of Cu-MC (OP) catalyst, CO₂ selectivity decreased, and CO selectivity increased with the increase in temperature. CH₄ selectivity does not change appreciably with the increase in temperature. All carbonaceous gas selectivity is almost constant throughout the temperature range for CuZn-MC (OP). CO₂ selectivity decreases and CO selectivity increases at a higher temperature between 300 and 350 °C for both CuCe-MC (OP) and CuCe-MC (IMP) catalysts. This result suggests that methanol decomposition and reverse water gas shift reactions occurred at higher temperatures [73]. Both Ce and Zn promoters favor reduction of CO at lower temperatures. The amount of CO produced at 250 °C for all promoted catalyst are less than 10%; this is superior to the Ni modifications that we discovered in our previous work, about 92% of CO when Ni was added to Cu catalyst [71]. CH_4 selectivity increased at a higher temperature for CuCe-MC (OP) catalyst. However, for the impregnated catalyst, CH₄ selectivity decreased at higher temperatures.

Table 4 shows the comparative studies of different copper-based catalysts with CuCe–MC (IMP) catalyst at 250 °C. It is difficult to compare them as there are distinct differences among the studies, especially in regard to the experimental conditions. Most of the methanol steam reforming (MSR) reactions using copper-based catalyst systems were performed at a different GHSV with H₂O to CH₃OH molar ratio that varied from 1 to 3.1. The higher methanol conversion of 75% was observed for the CuZnCe catalyst with a low GHSV of 1200 h⁻¹ at 250 °C [34]. The CuCe–MC (IMP) catalyst showed better activity than other copper-based catalysts at 250 °C (Figs. 11, 12).

3.2.3 Time-on-Stream Study of CuCe–MC (OP) Catalyst

To know the time-on-stream behavior of CuCe–MC (OP) catalyst, the MSR reaction was carried out for 50 h: reaction time at 300 °C, $H_2O/CH_3OH=3$ and GHSV=2900 h⁻¹. Methanol conversion decreases with time and it is almost stable after 22 h. Almost 30% conversion was observed after 22 h. The gas selectivity for all gases remained constant throughout time-on-stream studies.

3.2.4 Time-on-Stream Studies with CuCe–MC (IMP) Catalyst

To investigate the time-on-stream behavior for CuCe–MC (IMP) catalyst, the reaction was carried out for 42 h at 250 °C, $H_2O/CH_3OH=3$ and GHSV=2900 h⁻¹. Methanol conversion decreased with time, and it was almost stable after 22 h. Almost 40% methanol conversion was observed



Fig. 7 TGA-DSC analyses of all as-synthesized catalysts: a MC-As; b Cu-MC-As; c CuCe-MC-As; d CuZn-MC-As; e CuCe-MC-As (IMP)

after 22 h. The selectivity of all gases remained almost constant throughout the time-on-stream studies.

3.2.5 Spent Catalyst Characterization

Figure 13 shows the morphology of the CuCe–MC (OP) and CuCe–MC (IMP) after the completion of MSR studies. Based on the micrographs shown in Fig. 5c and e, it is apparent that the tiny particles observed in the fresh catalysts got agglomerated and the catalyst surface is covered with coke.

3.2.6 TGA–DSC Analysis of Spent Catalysts

Figure 14 shows TGA–DSC analyses of the spent catalysts. The analysis of coke-deposition over the catalyst surface was performed at atmospheric conditions. The TGA analysis results are in agreement with time-on-stream studies. The weight loss of ~8 and 18 wt% found in TGA analysis corresponds to the burning of moisture and graphitic carbon [77, 78]. The result suggests that CuCe–MC (OP) catalyst has high resistance to coke formation. The addition of CeO₂ in the catalysts decreased the carbon deposition during the MSR reaction. The weight loss is found less for one-pot



Fig. 8 XPS analyses of all catalysts after calcination: a C1s; b Cu2p; c Ce3d + Cu2p; d Zn2p



Fig. 9 Effect of reaction temperature on methanol conversion for Cu– MC (OP); CuCe–MC (OP); CuZn–MC (OP); CuCe–MC (IMP) catalysts (conditions: $H_2O/CH_3OH=3$; GHSV=2900 h⁻¹)

synthesis method, which reflects that the Cu (II) ions are well ordered in the lattice of CeO_2 [79].

Mesoporous carbon consists of meso and macro pores [80] and may result in more efficient catalysts in terms of selectivity towards products. Due to the presence of meso and macro pores, MC has different pore sizes. In contrast, mesoporous silica and titania have almost same pore size [13–15]. Various mesostructured carbons with different pore systems have been synthesized using a variety of different mesoporous silica templates [81–83]. The amorphous carbon in MC has temperature restraints, increasing the temperature above 400 °C can affect the hydrogen yield [31]. According to the TPR results, recorded at a temperature above 400 °C, MC possibly helps in the formation of methane due to the reaction between the carbonaceous support and H_2 [31].



Fig. 10 Effect of reaction temperature on the selectivity of product gases from the MSR reactions using Cu–MC (OP); CuCe–MC (OP); CuZn–MC (OP); CuCe–MC (IMP) catalysts (Conditions: $H_2O/CH_3OH=3$; GHSV=2900 h⁻¹)

Table 4Comparison of MSRactivity of CuCe–MC (IMP)with other copper loaded ceriaoxide materials at 250 °C	Catalyst	GHSV (h ⁻¹)	H ₂ O to CH ₃ OH molar ratio	CH ₃ OH Conver- sion (%)	References
	Cu/Ce _{0.75} Zr _{0.5} O ₂	21,000	2	48	[73]
	Au-Cu/ Ce _{0.75} Zr _{0.5} O ₂	21,000	2	45	[74]
	Cu/CeO ₂ /ZrO ₂	_	1	35	[75]
	CuO/ZnO/Al ₂ O ₃	24,000	3.1	67	[76]
	CuZnCe	1200	1.2	75	[34]
	CuCe-MC (IMP)	2900	3	68	This work

4 Conclusion

The Cu catalysts supported on mesoporous carbon, containing Ce and Zn, separately, were prepared using onepot synthesis and impregnation method. All catalysts exhibit mesoporous structures with high surface areas. The TPR results showed that the reducibility of the oxide nanoparticles of CuZn on MC (OP) catalyst was almost the same as Cu on MC (OP) catalyst, while CuCe–MC (IMP) catalyst showed two reduction peaks due to the reduction of CuO in two different environments. The catalyst activity was tested by varying the reaction temperature in the range of 200–350 °C. The CeO₂-modified catalysts prepared by one-pot synthesis and wetness impregnation methods both



Fig. 11 Time-on-stream MSR studies using CuCe–MC (OP) catalyst for 50 h (conditions: temperature 300 °C; $H_2O/CH_3OH=3$; GHSV=2900 h⁻¹)



Fig. 12 Time-on-stream MSR studies using CuCe–MC (IMP) catalyst for 42 h (conditions: temperature 250 °C; $H_2O/CH_3OH=3$; GHSV=2900 h⁻¹)

exhibited good performance in the steam reforming reactions. The optimum reaction temperature, in consideration of methanol conversion and H_2 selectivity, for Cu–Ce on MC (OP) is 300 °C, while the highest conversion and selectivity for Cu–Ce on MC (WI) was observed at 250 °C. The highest methanol conversion for Cu–Ce on MC (OP) and Cu–Ce on MC (WI) were 65 and 68%, respectively. All catalysts showed high hydrogen selectivity (>90%) in this temperature range. For the Zn-modified Cu–MC catalyst, a lower CO selectivity of less than 10% is observed even at temperatures over 300 °C. The analysis of the spent catalysts suggests that CuCe on MC (OP) catalyst has high resistance to coke formation and the addition of CeO_2 helps to decrease the carbon deposition during the reaction. Based on the performances of the catalysts in the long-term reactions, Ce-modified Cu–MC (WI) is more stable, indicating the deactivation of CuCe–MC (OP) is caused by both coke formation and sintering.



Fig. 13 SEM analyses of spent catalysts: a CuCe-MC (OP); b CuCe-MC (IMP)



Fig. 14 TGA–DSC analyses of spent catalysts: a CuCe–MC (OP); b CuCe–MC (IMP)

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