Ultrasonically assisted surface modified CeO$_2$ nanospindle catalysts for conversion of CO$_2$ and methanol to DMC

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ABSTRACT

This study developed a facile and effective approach to engineer the surface properties of cerium oxide (CeO$_2$) nanospindle catalysts for the direct synthesis of dimethyl carbonate (DMC) from CO$_2$ and methanol. CeO$_2$ nanospindles were first prepared by a simple precipitation method followed by wet chemical redox etching with sodium borohydride (NaBH$_4$) under high intensity ultrasonication (ultrasonic horn, 20 kHz, 150 W/cm$^2$). The ultrasonically assisted surface modification of the CeO$_2$ nanospindles in NaBH$_4$ led to particle collisions and surface reduction that resulted in an increase in the number of surface-active sites of exposed Ce$^{3+}$ and oxygen vacancies. The surface modified CeO$_2$ nanospindles showed an improvement of catalytic activity for DMC formation, yielding 17.90 mmol·g$^{-1}$ with 100% DMC selectivity. This study offers a simple and effective method to modify a CeO$_2$ surface, and it can further be applied for other chemical activities.

1. Introduction

Air pollution is an important cause of the greenhouse effect, which leads to climate change and global warming [1,2]. Carbon dioxide (CO$_2$), which is emitted upon the combustion of fuels such as natural gas, coal and petroleum from engines and industries [3,4], is reported to be the highest component in the greenhouse gases that are released into the earth’s atmosphere [2,3,5]. CO$_2$ is a stable molecule because it has a linear and centrosymmetric structure [6]. Generally, the transformation of CO$_2$ into other valuable products requires high energy input as the reactions are thermodynamically unfavorable (ΔH = 16.74 kJ·mol$^{-1}$) [7]. However, due to it being abundant, inexpensive, non-toxic, non-flammable and renewable [7-9], CO$_2$ is often used as a starting material in the chemical syntheses of compounds such as methane [10], methanol [11,12], formaldehyde [12], formic acid [10,12], formamides [13], methylamines [13], dimethyl ether (DME) [10,11], and dimethyl carbonate (DMC) [6-9].

DMC is an important organic compound [9,14,15] that is commonly used as an organic solvent and raw material in various chemical industries [7,14,15]. Its favorable biodegradability profile and its low toxicity to humans and the environment have made DMC into a green chemical that is suitable for sustainable production processes [14,16].

There are many applications of DMC including its role as a precursor in the synthesis of polycarbonate and isocyanate [14,17]. DMC can also be used as an electrolyte for lithium-ion batteries, as a fuel additive to increase octane number [18,19], as an intermediate in the synthesis of some antibacterial products, in veterinary drugs [20,21] and in pesticides [22,23]. Recently, the development of a green DMC production route has drawn interest as such a method can simultaneously fulfill industrial demand and tackle an environmental problem [17]. Several routes have been used for the synthesis of DMC, and traditional routes include the phosgene method, oxidative carbonylation, and the trans-esterification method [9]. In the phosgene method, highly toxic phosgene is used as a starting material and the byproduct, hydrogen chloride (HCl), can cause rapid reactor corrosion [24,25]. In oxidative carbonylation, methanol, oxygen, and carbon monoxide involved in the reaction are toxic and can be explosive [26,27]. Lastly, the transesterification method requires highly toxic chlorobenzene catalysts to catalyze the reaction [28,29]. Compared to these processes, the direct synthesis of DMC from methanol and CO$_2$ is seen as attractive as it is eco-friendly and produces only water (H$_2$O) as a byproduct [30-32]. However, due to thermodynamic limitations as shown, CO$_2$ + 2CH$_3$OH → (CH$_3$O)$_2$CO + H$_2$O (ΔG$^\circ$ = 26 kJ·mol$^{-1}$), the conversion reaction requires energy input and the DMC yield is relatively low [33-35]. Hence,
various metal oxide catalysts, for instance, K$_2$CO$_3$ [36,37], ZrO$_2$ [38,39], TiO$_2$ [40,41] and CeO$_2$ [19,42–44], have been used to increase the reaction rate and DMC formation. Cerium oxide (CeO$_2$) has become the dominant catalyst for the direct synthesis of DMC from CO$_2$ and methanol due to its high mass density, low thermal expansion, and good physical and chemical stability [45,46]. CeO$_2$ can shift easily between Ce$^{3+}$ and Ce$^{4+}$ [47], resulting in its rich surface oxygen vacancies and high oxygen storage capacity [48–51]. Although CeO$_2$ has good catalytic performance in some ways, its catalytic activity in DMC production still needs to be improved [52].

The key factors that affect the catalytic activity of CeO$_2$ are its morphology and surface properties. Cubic fluorite CeO$_2$ has various morphologies including different crystal planes and surface properties [53] that can directly affect the interaction between the adsorbed species and the surface-active sites [17,54,55]. Researchers investigated the influence of various morphologies of CeO$_2$ such as its cubic, rod, sphere, spindle and irregular shapes on catalytic activity. It was found that CeO$_2$ catalysts with spindle shape morphology showed better catalytic performance in the direct synthesis of DMC from CO$_2$ and methanol [8,17,34]. However, the excellent catalytic activity of CeO$_2$ nanospindle catalysts in the formation of DMC was suggested to be because the surface of each cubic fluorite CeO$_2$ spindle consisted of an active exposed (111) plane that had a large number of surface defect sites that could activate CO$_2$ and methanol, and also had a high potential to absorb CO$_2$ [8,17,48].

The catalytic activity of CeO$_2$ can also be improved by engineering its surface. The surface properties play a critical role in catalyst dispersion, stabilization and reactive gas adsorption–desorption [56–58]. The CeO$_2$ surface can be modified by increasing the number of surface active sites by varying specific surface areas, pore sites, the ratio of Ce$^{3+}$/Ce$^{4+}$, and the number of oxygen vacancies and acid-base sites [59]. There are many processes that can be used for modifying a CeO$_2$ surface, such as annealing under vacuum [60], hydrogen treatment [61], thermal activation [62], thermal annealing treatment [35,63], electron beam irradiation [64], and pressure control [65]. However, these processes are difficult to control and require expensive equipment and tools. Wet chemical redox etching is an interesting process for modifying a CeO$_2$ surface because it is a simple, inexpensive and effective process [66–69]. Chemical redox etching of CeO$_2$ nanorods with reducing agents such as sodium borohydride (NaBH$_4$) [66,68,69], ascorbic acid and hydrogen peroxide (H$_2$O$_2$) [67] produced superior catalytic activity in low temperature CO oxidation due to the formation of porous and rough surfaces, and an increase in specific surface areas, surface Ce$^{3+}$ fractions and concentration of oxygen vacancies [66–69]. The catalytic activity of CeO$_2$ in the CO oxidation reaction can further be improved after the chemical redox etching process by impregnation with active metals or metal oxides such as Pt [57], Ru [68], CuO [4,66,70], CoO$_x$, NiO$_x$, FeO$_x$, and MnO$_x$ [66]. These two-step treatments can effectively improve the dispersion of the impregnated species and also prevent the migration and aggregation of these active species on the surface of CeO$_2$. Wang et al. [66] reported that impregnation of CeO$_2$ nanorods with CuO after wet chemical redox etching with NaBH$_4$ to form CeO$_2$–CuO catalysts could enhance the catalytic activity for low temperature CO oxidation reaction due to the strong interfacial interaction between Cu ions and Ce ions resulting in the formation of surface-active sites through the oxidation–reduction reaction of Cu$^+ + Ce^{4+} \rightarrow Ce^{3+} + Ce^{3+}$. The surface modification of CeO$_2$ catalysts by wet chemical redox etching has been reported to be a simple and effective route for improving the catalytic activity. Furthermore, this interesting approach has not yet been applied and investigated in the modification of spindle shape CeO$_2$ catalysts for the direct synthesis of DMC from CO$_2$ and methanol. Therefore, in this work, we proposed a new strategy to engineer the surface properties of CeO$_2$ nanospindle catalysts using wet chemical redox etching process followed by incorporation of CuO active species by a wet impregnation process. Moreover, the treatment processes were improved using sono-assisted ultrasonication, in which the medium solution was irradiated with a high intensity ultrasonic waves of frequency 20 kHz–15 MHz and acoustic wavelength of 100 mm–100 μm to increase the surface reaction between CeO$_2$ nanospindles and the treatment reagents [71–73]. Finally, the characterization and investigation of the catalytic performance for the direct synthesis of DMC from CO$_2$ and methanol of these surface modified CeO$_2$ nanospindles was reported.

2. Material and methods

2.1. Synthesis of cerium oxide (CeO$_2$) nanospindles

CeO$_2$ was synthesized via a precipitation method. Firstly, 12 mmol of cerium(III) nitrate hexahydrate (Ce(NO$_3$)$_3$·6H$_2$O; purity 99.5 %, Carlo Erba) and 400 mmol of urea (CO(NH$_2$)$_2$; purity 99.0 %, Carlo Erba) were dissolved in 300 ml distilled water. The solution was ultrasonically irradiated with a low intensity ultrasonic wave (37 kHz, 80 W) in an ultrasonic bath at 70 °C for 1 h to obtain a white suspension. Next, the suspension was refluxed at 95 °C for 2 h in a round bottomed flask under magnetic stirring. After the reaction finished, the precipitates were centrifugally separated, dried overnight at 80 °C, and finally calcined in ambient air at 650 °C for 2 h.

2.2. Surface modification of CeO$_2$ nanospindles

The obtained CeO$_2$ nanospindles was chemically treated to modify their surface with a reducing agent, sodium borohydride (NaBH$_4$; purity 98.0 %, Acros organics) and copper(II) nitrate trihydrate (Cu(NO$_3$)$_2$·3H$_2$O; purity 99.0 %, Carlo Erba) with the assistance of a high intensity ultrasonic wave. Firstly, 1.000 g of CeO$_2$ was dispersed in 194 ml distilled water in a sonochemical reaction vessel. The suspension was then ultrasonically irradiated with a high intensity ultrasonic wave (Tihorn, 20 kHz, 150 W/cm$^2$ Sonics Model VZ 750, VibraCell) for 2 min. Next, 6 ml of 4 M NaBH$_4$ or 5 wt% of Cu(NO$_3$)$_2$·3H$_2$O was added and the suspensions were continuously irradiated until the 30 min mark. After that the products were centrifugally separated, dried overnight at 80 °C, and finally calcined in air at 400 °C for 2 h to create a strong interaction between B- species and CeO$_2$ surface and to convert Cu- species into oxide form. The catalysts after chemical treatment with NaBH$_4$ and Cu(NO$_3$)$_2$·3H$_2$O were labeled as CeO$_2$-B and CeO$_2$-CuO, respectively. CeO$_2$-H$_2$O catalyst was prepared via the same procedure except that the CeO$_2$ was treated in de-ionized water under a high intensity ultrasonication. The CeO$_2$-B-CuO catalyst was chemically treated in two-step with 4 M NaBH$_4$ followed by 5 wt% of Cu(NO$_3$)$_2$·3H$_2$O and after the treatment processes, the products were calcined only once at 400 °C for 2 h. Notably, NaBH$_4$ was chosen as a reducing agent in the work as it is a strong and effective reducing agent that is commonly used in laboratory and industrial applications.

2.3. Characterization

Catalyst morphology was determined by scanning electron microscope (SEM; FEI Quanta 250, samples preparation with gold (Au) coating) and transmission electron microscope (TEM; FEI Tecnai G2 20). Elemental composition was investigated with an energy-dispersive spectroscopy (EDS, Oxford Instrument X-max 20) equipped with SEM. The particle size was estimated by measuring the size of at least 50 particles in SEM images using the ImageJ program. The powder X-ray diffraction (XRD) patterns were recorded on a Rigaku Smartlab diffractometer with a CuKα (40 kV, 30 mA) radiation at the diffraction angle (2θ) range of 5–90° with a scanning rate of 20.00° min$^{-1}$ and indexing from the JCPDS (ICDD) database. Debye-Scherrer’s equation shown in Eq. (1) was used for calculation of the crystallite size ($D$) [74]:

$$D = \frac{k \lambda}{\beta \cos \theta}$$

Where $D$ is the crystallite size, $k$ is the shape factor (value 0.9), $\lambda$ is the wavelength of X-ray (1.54056 Å), $\beta$ is the full width at half maximum (fwhm) for the most intense peak, and $\theta$ is the diffraction angle.
where k is a constant taken as 0.94, λ is X-ray wavelength (CuKα radiation 0.15418 nm), $\beta_{\text{full}}$ is the full width at half maximum (FWHM) of intensity of the diffraction peak, $hkl$ are the Miller indices of the planes being analyzed, and $\theta$ is the diffraction angle. The lattice constant (a) was calculated from the Bragg equation and the crystal spacing formula as shown in Eq. (2) and Eq. (3) [52,73]:

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

$$2\sin\theta = n\lambda$$

where n is the reflection series and $d_{hkl}$ is the crystal spacing. Molecular structure of the catalysts was analyzed using a Fourier transform infrared spectrometer (FT-IR; Perkin Elmer, Spectrum Gx) and Raman spectrometer (Thermo Scientific, DXR Smart, 532 nm excitation solid state laser in the range of 200–1500 cm$^{-1}$). The Brunauer-Emmett-Teller (BET) specific surface area was tested by nitrogen adsorption–desorption with Autosorb (Autosorb 1). X-ray photoelectron spectroscopy (XPS; Kratos, Amicus with MgKα anode 20 mA and 10 kV) was employed to estimate the surface states of elemental composition by Gaussian fitting the XPS spectra using MagicPolt program. Ammonia (NH$_3$) employed to estimate the surface states of elemental composition by desorption with Autosorb (Autosorb 1). The lattice parameters and crystallite sizes using the Debye Scherrer equation [74] of all catalysts are shown in Table 1. The lattice parameter and crystallite size of unmodified CeO$_2$ were 5.4165 ± 0.0022 Å and 19.36 ± 3.28 nm, respectively. After the surface modification, the lattice parameter and crystallite size tended to decrease, varying between 5.4109 and 5.4121 Å and 16.81–19.56 nm. The decrease of both lattice parameter and crystallite size after modification of the CeO$_2$ surface could have been related to the formation of surface defects caused by two major factors, firstly, the collision of catalyst particles due to an acoustic cavitation stimulated by high intensity ultrasonic irradiation [78–82] and secondly, the reduction of Ce$^{4+}$ to Ce$^{3+}$ due to the redox reaction of CeO$_2$ surface with NaBH$_4$ reducing agent and Cu-species, which consequently led to the formation of oxygen vacancies to maintain charge neutrality in the ionic structure [31,52,66]. Even though Ce$^{3+}$ has a slightly larger ionic radius than Ce$^{4+}$ (ionic radius with 8-fold coordination of Ce$^{3+}$ = 1.143 Å and Ce$^{4+}$ = 0.97 Å), the increase of surface oxygen vacancy concentration seemed to have a bigger effect as it decreased the effective anionic radius in the fluorite lattice, which resulted in the variation of the lattice parameter [81,83].

The XRD patterns of CeO$_2$ and surface modified CeO$_2$ catalysts with de-ionized water (CeO$_2$–H$_2$O), NaBH$_4$ (CeO$_2$–B), CuO (CeO$_2$–CuO) and two-step treatment with NaBH$_4$ followed by CuO (CeO$_2$–B-CuO) and high intensity ultrasonic irradiation are illustrated in Fig. 1. All catalyst peaks were indexed to the face centered cubic CeO$_2$ of fluorite structure (JCPDS 00–034–0394, space group Fm$3$m (225)) [17,52]. All catalysts had good crystallinity, demonstrating that modification with NaBH$_4$ and/or CuO had not altered the original fluorite-type structure of CeO$_2$.

There was no diffraction peak related to B- and Cu- phases observed in the XRD patterns of CeO$_2$–B, CeO$_2$–CuO and CeO$_2$–B-CuO catalysts and this was probably because only low concentrations of B- and Cu-species existed in the CeO$_2$ based catalysts. The calculated lattice parameters and crystallite sizes using the Deybe Scherrer equation [74] of all catalysts are shown in Table 1. The lattice parameter and crystallite size of unmodified CeO$_2$ were 5.4165 ± 0.0022 Å and 19.36 ± 3.28 nm, respectively. After the surface modification, the lattice parameter and crystallite size tended to decrease, varying between 5.4109 and 5.4121 Å and 16.81–19.56 nm. The decrease of both lattice parameter and crystallite size after modification of the CeO$_2$ surface could have been related to the formation of surface defects caused by two major factors, firstly, the collision of catalyst particles due to an acoustic cavitation stimulated by high intensity ultrasonic irradiation [78–82] and secondly, the reduction of Ce$^{4+}$ to Ce$^{3+}$ due to the redox reaction of CeO$_2$ surface with NaBH$_4$ reducing agent and Cu-species, which consequently led to the formation of oxygen vacancies to maintain charge neutrality in the ionic structure [31,52,66]. Even though Ce$^{3+}$ has a slightly larger ionic radius than Ce$^{4+}$ (ionic radius with 8-fold coordination of Ce$^{3+}$ = 1.143 Å and Ce$^{4+}$ = 0.97 Å), the increase of surface oxygen vacancy concentration seemed to have a bigger effect as it decreased the effective anionic radius in the fluorite lattice, which resulted in the variation of the lattice parameter [81,83].

The FT-IR spectra of the CeO$_2$ and surface modified CeO$_2$ catalysts in the range of 400–4000 cm$^{-1}$ are shown in Fig. 2. The spectra of all catalysts showed the characteristic absorption bands of Ce-O stretching vibration at 565 cm$^{-1}$ [84]. The complex bands observed at 1300 and 1050 cm$^{-1}$ correlated with the adsorption of carbonate species (CO$_3^2$) on the surface, which might have formed during the preparation process.
After the surface modification with \( H_2O \), nanospindles had simply been prepared via a precipitation method. Catalysts, especially in the case of CeO\(_2\), were also observed at 988 and 798 cm\(^{-1}\), and this could have been because there had been an increase in the number of surface-active sites that absorbed foreign species after surface modification under a high-intensity ultrasonic irradiation. In the case of the CeO\(_2\)-B and CeO\(_2\)-B-CuO catalysts, the absorption bands of B-O asymmetric and symmetric stretching vibrations were observed at 988 and 798 cm\(^{-1}\), respectively [91–93], indicating the presence of B-species in these catalysts.

The morphology of the catalysts was investigated by SEM and TEM, and the results are shown in Figs. 3 and 4, respectively. The average particle sizes obtained by measuring width at center and length of catalyst particles observed in the SEM images are summarized in Table 1. Before the surface modification (Figs. 3(a) and 4(a)), CeO\(_2\) consisted in spindle-shaped particles with width at center of 1.38 ± 0.42 \( \mu m \) and length of 5.53 ± 1.42 \( \mu m \). The edges of the spindles were curved, and the ends were pointy, indicating the existence of defect sites [17]. The results from the XRD and SEM study confirmed that the CeO\(_2\) nanospindles had simply been prepared via a precipitation method. After the surface modification with H\(_2\)O, NaBH\(_4\) and CuO under high intensity ultrasonic irradiation, significant changes on the catalyst surface, such as surface roughness or pore formation, could not be seen clearly in the SEM (Fig. 3(b)–(e)) and TEM images (Fig. 4(b)). However, some imperfect spindles and debris were observed in SEM images of the surface modified catalysts CeO\(_2\)-H\(_2\)O, CeO\(_2\)-B, CeO\(_2\)-CuO and CeO\(_2\)-B-CuO (Fig. 3(b)–(e)). Particle collision induced by acoustic cavitation (the formation, growth, and collapse of microbubbles) created a microjet effect which led to particle breakage [78–80,94] and thus resulted in the decrease of average particle size, as shown in Table 1.

The SEM image, EDS spectrum and elemental mapping of the two-step treatment CeO\(_2\)-B-CuO catalyst are presented in Fig. 5. The EDS spectrum confirmed that the CeO\(_2\)-B-CuO catalyst consisted of Ce, O, B and Cu elements. The elemental mappings showed that the B- and Cu-species were uniformly dispersed throughout the CeO\(_2\) phase. As in the preparation processes, the surface modified CeO\(_2\) catalysts were calcined in air at 400 °C for 2 h after the chemical treatment with NaBH\(_4\) and Cu(NO\(_3\))\(_2\)-3H\(_2\)O, so the B- and Cu-species were more likely to exist as nanocrystalline B\(_2\)O\(_3\) and CuO on CeO\(_2\) surface.

The specific surface areas of catalysts obtained through nitrogen adsorption–desorption measurements are shown in Table 1. The surface area of CeO\(_2\) nanospindles was 65.56 m\(^2\) g\(^{-1}\), and it increased to 75.21 m\(^2\) g\(^{-1}\) (CeO\(_2\)-H\(_2\)O), 70.17 m\(^2\) g\(^{-1}\) (CeO\(_2\)-B) and 79.32 m\(^2\) g\(^{-1}\) (CeO\(_2\)-CuO) after the surface modification. The increase of surface area after the surface modification agreed well with the reduction of particle size caused by particle collisions stimulated by high intensity ultrasonic irradiation. In the case of the CeO\(_2\)-CuO catalyst, the highest specific surface area at 79.32 m\(^2\) g\(^{-1}\) could have presented due to the contribution of the high specific surface area phase of nanocrystalline CuO. In the case of the CeO\(_2\)-B-CuO catalyst, the surface area had decreased to 50.50 m\(^2\) g\(^{-1}\). This may have been due to redox etching agent NaBH\(_4\) creating defect sites on the surface of CeO\(_2\), which led to strong interfacial bonding between the defect sites and nanocrystalline CuO, thus resulting in the decrease of specific surface area of the CeO\(_2\)-B-CuO catalyst [57,66,95,96].

Raman spectroscopy was performed to study the defects in the catalyst structures. The Raman spectra of CeO\(_2\) and surface modified CeO\(_2\) nanospindle catalysts (Fig. 6) showed the characteristic Raman active bands of CeO\(_2\) at ~ 464 cm\(^{-1}\), typical of the triply degenerate \( F_{2g} \) vibrational modes of fluoride-type structures [52]. The weak bands around 255 and 600 cm\(^{-1}\) were assigned to the doubly degenerate TO \((2TA)\) and the defect-induced band \((D\) band), respectively [52,66]. The Raman active bands related to peroxide species (\( O_2^2^-\) ) were also observed around 831 cm\(^{-1}\) [66] and the intensity of these bands tended to decrease after the surface modification. When considered the characteristic \( F_{2g} \) bands, the band intensities were found to decrease after the surface modification and the Raman shift of these \( F_{2g} \) bands was 464, 463, 457 and 456 cm\(^{-1}\) for CeO\(_2\), CeO\(_2\)-H\(_2\)O, CeO\(_2\)-B, CeO\(_2\)-CuO and CeO\(_2\)-B-CuO, respectively, indicative of red shift after the surface modification. The decrease of the \( F_{2g} \) band intensity and Raman shift position after the surface modification could be attributed to the variation of Ce-O bond length in the fluorite crystal due to a partial reduction of the smaller ionic radius Ce\(^{3+}\) cations to larger Ce\(^{4+}\) cations [52,97,98], as well as the decrease of crystallite size caused by the formation of defect sites on the CeO\(_2\) surface [52,67]. The results of the Raman study were consistent with the change in crystal lattice as observed in the XRD analysis.

The surface states of CeO\(_2\) and surface modified CeO\(_2\) nanospindle catalysts were further analyzed using the XPS technique. The Ce 3d spectra, each composed of 10 peaks, are shown in Fig. 7. The 10 peaks were assigned to V \( 2p_3/2 \) and U \( 2p_1/2 \), corresponding to the spin–orbit multiplets of Ce \( 3d_{5/2} \) and Ce \( 3d_{3/2} \) respectively [52,99]. The peaks V \( ^1S \) (881.18 eV), V \( ^3P \) (886.79 eV), U \( ^1S \) (900.38 eV) and U \( ^3P \) (904.44 eV) belonged to the Ce\(^{3+}\) state, while the peaks V \( ^3S \) (883.47 eV), V \( ^1P \) (890.37 eV), V \( ^3P \) (898.69 eV), U \( ^3S \) (902 eV), U \( ^1P \) (907.94 eV) and U \( ^3P \) (917.47 eV) belonged to the Ce\(^{4+}\) state [66]. The O 1 s spectra for all catalysts are illustrated in Fig. 8. In the literature, three types of peaks in the integral fitting of the O 1 s spectrum were commonly ascribed to three oxygen species: lattice oxygen \( O_2^2^-\), oxygen vacancy \( O_2^-\), and surface-chemisorbed oxygen species or oxygen in hydroxyl groups (Oc). The peaks at 529.7, 531, and 532.5 eV were assigned to \( O_2^2^-\), \( O_2^-\), and \( O_C\) on the catalyst surface.

| Catalyst | Lattice parameter (Å) | Crystal size (nm) | Particle size (μm) | Surface area (m² g⁻¹) |
|----------|----------------------|------------------|-------------------|----------------------|
|          |                      |                  | Width | Length |                  |
| CeO\(_2\) | 5.4165 ± 0.0022 | 19.36 ± 3.28 | 1.36 ± 0.553 | 56.56 |
| CeO\(_2\)-H\(_2\)O | 5.4121 ± 0.0030 | 17.39 ± 4.66 | 1.16 ± 4.98 | 75.21 |
| CeO\(_2\)-B | 5.4113 ± 0.0048 | 16.81 ± 3.62 | 0.81 ± 4.24 | 70.17 |
| CeO\(_2\)-CuO | 5.4109 ± 0.0025 | 19.07 ± 3.81 | 1.08 ± 4.94 | 79.32 |
| CeO\(_2\)-B-CuO | 5.4118 ± 0.0036 | 19.56 ± 4.96 | 1.21 ± 5.07 | 50.50 |
| CuO | 0.0036 | 0.36 | 1.26 |  |

Fig. 2. FTIR spectra of CeO\(_2\) and surface modified CeO\(_2\).

Table 1
Crystal properties, particle size and surface area of CeO\(_2\) and surface modified CeO\(_2\).

![Image of Table 1](image-url)
respectively [66]. For the CeO$_2$-B catalyst, the O$_C$ peak appeared slightly shifted to higher binding energy, and this could indicate the presence of another oxygen type of B-O which was typically observed at 533.2 eV [100]. In case of CeO$_2$-CuO and CeO$_2$-B-CuO, the O$_C$ peaks slightly had shifted to lower binding energy. A possible reason for the shift of the O$_C$ peaks could have been the contribution from the O$_C$(Cu$^{2+}$) of CuO phase, which was generally observed at 529 eV [101].

The quantitative assessment of the surface concentrations of Ce$^{3+}$ ([Ce$^{3+}$]) and Ce$^{4+}$ ([Ce$^{4+}$]) in the total Ce content was estimated from the total integrated areas of the Gaussian fitting peaks using Eq. (7) and Eq. (8) [102]. The proportion of O$_V$ to the total surface oxygen species ([O$_V$]) was estimated using Eq. (9) [103]:

Fig. 3. SEM images of (a) CeO$_2$, (b) CeO$_2$-H$_2$O, (c) CeO$_2$-B, (d) CeO$_2$-CuO and (e) CeO$_2$-B-CuO.

Fig. 4. TEM images of (a) CeO$_2$ and (b) CeO$_2$-B.
The surface concentration fractions of Ce\(^{3+}\), Ce\(^{4+}\) and O\(_v\) on the CeO\(_2\) and surface modified CeO\(_2\) catalysts are shown in Table 2. The [Ce\(^{3+}\)] of CeO\(_2\) nanospindles was 9.06 %, and it increased to 9.61 %, 14.03 %, 10.16 % and 10.71 % for CeO\(_2\)-H\(_2\)O, CeO\(_2\)-B, CeO\(_2\)-CuO and CeO\(_2\)-B-CuO, respectively. The increase of [Ce\(^{3+}\)] was consistent with changes in oxygen vacancy concentration, [O\(_v\)], from 20.81 % to 26.37–48.70 % after the surface modification since the reduction of Ce\(^{4+}\) to Ce\(^{3+}\) species resulted in the generation of oxygen vacancies to manage charge balance [99,104]. The increase of defect sites after the surface modification was due to the synergistic effects of the increase of surface-active area caused by particle collisions induced by the high intensity ultrasonic irradiation together with the reduction of Ce\(^{4+}\) to Ce\(^{3+}\) from the redox reaction with NaBH\(_4\) and CuO, as previously discussed. According to Table 2, CeO\(_2\)-B prepared by chemical redox etching with NaBH\(_4\) possessed the highest [Ce\(^{3+}\)] and [O\(_v\)] defect sites.
The increase of oxygen (O\(^{2-}\)) of CeO\(_2\) and CeO\(_2\)-CuO catalysts [66,95]. This observation agreed well with the intensity reduction of the Raman active band of peroxide species after the surface modification as shown in Fig. 5. As the exposed Ce\(^{3+}\) coupled with oxygen vacancies on surface of CeO\(_2\) catalysts were reported to be the active sites for the direct synthesis of DMC from CO\(_2\) and methanol [52,57,95], modification of the CeO\(_2\) surface with the NaBH\(_4\) redox etching under a high intensity ultrasonication appeared to be an effective method to engineer the surface characteristics and possibly improve the catalytic activities of CeO\(_2\) catalysts.

\[
\text{NaBH}_4 + 2\text{H}_2\text{O} \rightarrow \text{NaBO}_2 + 4\text{H}_2(10) \\
\text{BO}_2^- + \text{O}_2^- \rightarrow \text{BO}_3^- + \text{O}_2^-(11)
\]

The NH\(_3\) and CO\(_2\) adsorption were examined to investigate the acid-base properties of the CeO\(_2\) and surface modified CeO\(_2\) nanospindle catalysts. Fig. 9 (a) and (b) show the NH\(_3\) and CO\(_2\)-TPD profiles of all catalysts from 50 to 950 °C, respectively. The weak, moderate, and strong acid and basic sites were evaluated from the NH\(_3\) and CO\(_2\)-TPD desorption peak areas at < 200 °C, 200–400 °C and > 400 °C, respectively [6–8]. The acidity and basicity of all catalysts are summarized in Table 3. CeO\(_2\) and surface modified CeO\(_2\) nanospindle catalysts can behave as bi-functional acid-base catalysts since their surface consists of both acidic and basic sites [7], which are required for the conversion of CO\(_2\) and methanol to DMC [6–8]. The total acidity of CeO\(_2\) nanospindles was 1.542 mmol.g\(^{-1}\) while the total basicity was 0.474 mmol.g\(^{-1}\). After the surface modification, the total acidity and basicity were found to have decreased to 0.739–0.905 mmol.g\(^{-1}\) and 0.241–0.369 mmol.g\(^{-1}\), respectively. Notable, the total acidity and basicity obtained in this study were comparable to those reported in the literature, in which the reported acidity and basicity values of CeO\(_2\) catalysts varied between 0.25 and 0.63 and 0.08–0.73 mmol/g, respectively [8,17,103,105,106]. The decrease of acid and basic sites after the surface modification was inconsistent with the increase of surface oxygen vacancy concentration that was observed from other characterization techniques. Generally, oxygen vacancies serve as the Lewis acid sites on the CeO\(_2\) surface, and the formation of oxygen vacancies consequently creates low coordinated oxygen anions which typically act as the Lewis basic sites [7,43]. The variation in acid-base properties observed in this study may have occurred due to the complex interaction of different types of surfaces species i.e., Ce\(^{3+}\)/Ce\(^{3+}\), oxygen, B- and Cu- species with the surface adsorbrates [8,103,105,106].

The increase of [O\(_{\text{v}}\)] of CeO\(_2\)-B catalyst suggested the relation between the B- species and the oxygen vacancy defects [66] in which the increase of O\(_{\text{v}}\) concentration might have been related to the formation of active oxygen (O\(^{2-}\)) caused by the reaction of borate (BO\(^{2-}\)) species as shown in Eqs. (10) and (11) [66,95]. In these reactions, sodium metaborate (NaBO\(_2\)) could have formed through the hydrolysis of NaBH\(_4\) to create the BO\(^{2-}\) species. Subsequently, the BO\(^{2-}\) species reacted with the absorbed peroxide species (O\(^{2-}\)) on the surface of CeO\(_2\). The reaction between BO\(^{2-}\) and O\(^{2-}\) was not only consuming the inactive peroxide species, but also enhancing the active oxygen (O\(^{2-}\)) on the surface of CeO\(_2\)-B and CeO\(_2\)-B-CuO catalysts [66,95].

Table 2

| Catalyst       | [Ce\(^{3+}\)] (%) | [Ce\(^{4+}\)] (%) | [Ce\(^{3+}$/Ce\(^{4+}\)] (%) | [O\(_{\text{v}}\)] (%) |
|----------------|-------------------|-------------------|-----------------------------|-----------------------|
| CeO\(_2\)      | 90.94             | 9.06              | 9.97                        | 20.81                 |
| CeO\(_2\)-H\(_2\)O | 90.39             | 9.61              | 10.63                       | 26.37                 |
| CeO\(_2\)-B    | 85.97             | 14.03             | 16.32                       | 48.70                 |
| CeO\(_2\)-CuO  | 89.84             | 10.16             | 11.31                       | 29.30                 |
| CeO\(_2\)-B-CuO| 89.29             | 10.71             | 11.99                       | 41.74                 |

Fig. 8. XPS spectra of O 1 s of CeO\(_2\) and surface modified CeO\(_2\).

Fig. 9. TPD of (a) NH\(_3\) and (b) CO\(_2\)-TPD profiles of CeO\(_2\) and surface modified CeO\(_2\).
Catalytic activity of CeO₂ and oxygen vacancies has been said to promote CO₂ under high intensity ultrasonication [66]. The increase of surface Ce₂O₃ selectivity are presented in Table 4 and Fig. 10. The catalytic activity tests for the direct synthesis of DMC from CO₂ and methanol were performed over the CeO₂ and surface modified CeO₂ nanospindle catalysts. The DMC yield, methanol conversion, TOF and DMC selectivity are presented in Table 4 and Fig. 10. The catalytic activity tests showed that CeO₂ nanospindles that had been simply prepared by a precipitation method could catalyze the direct synthesis of DMC from CO₂ and methanol by providing high DMC yield at 14.44 mmol·g⁻¹, methanol conversion at 0.29 %, TOF at 0.43 h⁻¹ and 100 % DMC selectivity with only DMC, the remaining methanol, and by-product water contained in the liquid products. It should be noted that the % methanol conversion reported in this study was relatively low, which was because a high quantity of methanol feedstock at 40 ml was used in the reaction. After the surface modification, all catalysts showed higher performances than the unmodified CeO₂, and the order of performance was CeO₂-B > CeO₂-B-CuO > CeO₂-CuO > CeO₂-H₂O > CeO₂. The DMC yield of CeO₂-H₂O was higher than the unmodified CeO₂ at 15.45 mmol·g⁻¹, indicating that just the irradiation of the surface of CeO₂ nanospindles with a high intensity ultrasonic wave in deionized-water was able to increase the surface-active sites and consequently enhance the catalytic activity [107]. Among the modified surface catalysts, CeO₂-B exhibited the highest DMC yield at 17.90 mmol·g⁻¹, 0.36 % methanol conversion, and TOF at 0.54 h⁻¹. The improvement of catalytic performance of CeO₂-B correlated with the rise of the concentration fraction of surface-active sites of exposed Ce³⁺ and oxygen vacancies caused by the chemical redox etching with NaBH₄ under high intensity ultrasonication [66]. The increase of surface Ce³⁺ and oxygen vacancies has been said to promote CO₂ and methanol adsorption, which are responsible for the increase of DMC yield formation [103]. The DMC yields of CeO₂-CuO (15.80 mmol·g⁻¹) and CeO₂-B-CuO (16.47 mmol·g⁻¹) were lower than that of CeO₂-B, but still higher than those of the unmodified CeO₂ and CeO₂-H₂O. This showed that the dispersion of nanocrystalline CuO on the CeO₂ surface was able to improve the catalytic activity due to the interaction between Cu ions and Ce ions and the formation of surface defect sites through the oxidation-reduction reaction of Cu⁺ + Ce⁴⁺ ↔ Cu²⁺ + Ce³⁺. [31,52,58]. However, the effect of CuO on the improvement of catalytic activity of CeO₂ was lower when compared to that resulting from the chemical redox etching with NaBH₄. In case of CeO₂-B-CuO, treating the CeO₂ surface with NaBH₄ before impregnating with CuO led to strong interfacial bonding between the surface defect sites and the CuO species, which resulted in the reduction of surface-active area and did not enhance the DMC formation as much as expected.

The mechanism for DMC formation from CO₂ and methanol over the CeO₂-B catalyst is shown in Fig. 11. Firstly, a CeO₂-B catalyst was prepared by surface modification of CeO₂ nanospindles with a strong reducing agent, NaBH₄, under a high intensity ultrasonic irradiation in order to create surface-active sites of exposed Ce³⁺ and oxygen vacancies that could serve as Lewis acid sites [66,78,103]. The DMC formation began when CO₂ molecules were adsorbed onto the CeO₂-B surface through the Lewis acid-base interaction of oxygen vacancies on the catalyst surface and nonbonding electrons in the oxygen atoms of CO₂ [103,106]. Then, methanol molecules were adsorbed onto adjacent Ce³⁺ Lewis acid sites through the oxygen atoms of CH₃OH to form intermediate methoxy carbonyl ions (CH₃OCO₂). After that, other methanol molecules were adsorbed on the opposite Ce²⁺ sites [43]. Next, H atoms from methanol molecules and O atoms in CO₂ molecules were removed through the Lewis acid-base reaction to create DMC and water by-product. Finally, oxygen vacancies were released onto the catalyst surface [106].

Table 5 presents a comparison of the catalytic performance of CeO₂-based catalysts for the direct synthesis of DMC from CO₂ and methanol which involved similar systems to the ones used in this study. The surface modified CeO₂-B nanospindle catalysts prepared in this study showed higher DMC yields than those previously reported. These results suggested that chemical treatment of CeO₂ nanospindle surface with a redox etching reagent, NaBH₄, under a high intensity ultrasonication

| Catalyst | DMC yield (mmol) | DMC yield (mmol·g⁻¹) | Methanol Conversion (%) | TOF (h⁻¹) | DMC selectivity (%) |
|----------|-----------------|----------------------|------------------------|-----------|-------------------|
| CeO₂     | 1.44            | 14.44                | 0.29                   | 0.43      | 100               |
| CeO₂-H₂O | 1.54            | 15.45                | 0.31                   | 0.46      | 100               |
| CeO₂-B   | 1.79            | 17.90                | 0.36                   | 0.54      | 100               |
| CeO₂-CuO | 1.58            | 15.80                | 0.32                   | 0.47      | 100               |
| CeO₂-B-CuO | 1.65           | 16.47                | 0.33                   | 0.49      | 100               |

Fig. 10. Correlation between DMC yield and methanol conversion of CeO₂ and surface modified CeO₂.
was a simple and effective method to enhance the catalytic activity of CeO$_2$ nanospindles for the production of DMC.

4. Conclusion

In this study, we reported a simple and effective method that can be used to modify the surface properties of CeO$_2$ nanospindles via an ultrasonically assisted wet chemical redox etching. The CeO$_2$ nanospindles were first prepared via a precipitation method, and this was followed by chemical treatment with a strong reducing agent, NaBH$_4$, and/or Cu solution under high intensity ultrasonic irradiation. The particle collisions and surface reduction induced by the sonochemical effect and redox reaction resulted in an increase of surface-active sites of exposed Ce$^{3+}$ and oxygen vacancies. CeO$_2$-B showed the highest catalytic activity for the conversion of CO$_2$ and methanol to DMC, which corresponded well with the increased number of surface-active sites capable of absorbing reactant species and subsequently participating in the formation reaction. These results suggest that the ultrasonically assisted wet chemical redox etching is a simple and effective method to engineer the surface properties of CeO$_2$ catalysts.

Declararion of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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