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Microwave-assisted synthesis of highly dispersed ZrO$_2$ on CNTs as an efficient catalyst for producing 5-hydroxymethylfurfural (5-HMF)

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dispersion of the supported ZrO$_2$, which affects the performance of the catalyst. For instance, Li et al. [17] synthesized ZrO$_2$/SBA-15 catalysts using the mesoporous SBA-15 with high specific surface area (600–1000 m$^2$·g$^{-1}$) as support, and the mesoporous structure of SBA-15 enabled ZrO$_2$ to be uniformly dispersed on the surface of the support to form a monodisperse ZrO$_2$ phase with the particle size of $<$10 nm. The uniform dispersion and small particles promoted the exposure of the active sites on ZrO$_2$, extremely improving the catalytic activity of the catalyst. In detail, $\sim$92.6% conversion was achieved by using the supported ZrO$_2$ in the esterification reaction of pyrolysis oil, which was much higher than that of the conventional bulk ZrO$_2$ catalyst.

Due to the large specific area and excellent chemical and physical stability, carbon nanotubes (CNTs), such as multi-walled (MWCNTs) and single-walled (SWCNTs) are widely used as the catalyst supports for preparing supported catalysts [18,19]. Especially in hydrothermal synthesis, with the aim to make the ZrO$_2$ particles more uniformly distributed on the surface of CNTs and prevent particle aggregation, surface modification is usually required to increase the number of functional groups (such as $-$COOH, $-$OH, and $-$C$=$O) on the surface of CNTs, which can act as nucleation sites for anchoring ZrO$_2$ [20–23]. For example, Liu et al. [14,24] used nitric acid to functionalize the surface of MWCNTs and introduced a large number of oxygen-containing functional groups (–COOH, $-$OH, and $-$C$=$O) on the surface of MWCNTs, facilitating uniform growth of ZrO$_2$ particles on MWCNTs. Besides, the C K-edge NEXAFS characterization showed that the oxygen-containing groups on MWCNT interact with Zr precursor during the hydrothermal synthesis (at 180 °C and 20 atm for 6 h) to form a strong C–O–Zr bond between ZrO$_2$ and MWCNTs, improving the stability of the supported ZrO$_2$ catalyst on MWCNTs. In contrast, ZrO$_2$ was prone to agglomerate on the surface in the hydrothermal synthesis with unmodified MWCNTs as catalyst support. Notably, although previous studies have demonstrated the effectiveness of using versatile CNTs to control the size of supported zirconia, the current hydrothermal methods for preparing the zirconia nanoparticle-CNTs composite catalyst are rather harsh, time- and energy-consuming.

Compared to the classic contact heating that relies on heat conduction and convection, microwave (MW)-induced heating has its unique advantage, such as high heating efficiency, selectively heating, and microwave-induced ‘hot spot’ effect [25]. With the mentioned advantages, microwave irradiation has become a means of process intensification in material synthesis and chemical reactions [26]. For example, MW irradiation could accelerate the synthesis of MIL-88 significantly, reducing the synthetic time from several days required in conventional hydrothermal synthesis to several minutes [27]. Similarly, benefiting from the rapid heating, the particle size of MIL-88 synthesized by MW-assisted method (about 0.2 μm) is smaller than that of conventional hydrothermal method (>2 μm). Furthermore, the MW-assisted synthesis can be further enhanced when the MW-absorbing material is used to form “hot spot” [28]. In previous work, the highly MW-absorbing SiC was preferentially heated by MW, which enabled the selective growth of uniform ZSM-5 on the SiC surface and suppressed the formation of ZSM-5 crystals in the liquid phase [29]. Particularly, carbon materials (including CNTs) are considered as excellent microwave absorbers due to their large dielectric constants (ranging from 3 to 16) [30,31]. Therefore, accordingly, when considering the preparation of supported ZrO$_2$ on CNTs, MW-assisted synthesis would be a rational choice to intensify the synthesis and control the property of the supported ZrO$_2$. In this paper, we used the MW-hydrothermal method to synthesize highly dispersed nano-zirconia-loaded ZrO$_2$/MWCNTs composite catalysts with tiny particle diameters through the “hot spot” effect to provide a powerful catalyst for the catalytic conversion of fructose to 5-HMF. According to conventional hydrothermal synthesis methods, carboxyl groups on the surface of CNTs are necessary to provide nucleation sites for anchoring ZrO$_2$ on CNTs [32]. Therefore, the MWCNTs with carboxyl groups were used in this work. Meanwhile, the structures of catalysts were characterized and compared with catalysts from conventional hydrothermal synthesis, in order to further reveal the mechanism of MW-hydrothermal synthesis and provide a paradigm for understanding the application of MW induced “hot spots” in the synthesis of catalysts. Finally, the model reaction of selective catalytic dehydration of fructose to 5-hydroxymethylfurfural (5-HMF) was used to evaluate the catalytic activity of the developed ZrO$_2$/MWCNTs composite catalysts.

2. Experimental

2.1. Materials and chemicals

—COOH functionalized MWCNTs (MWCNTs(C), average diameter of 8–15 nm, length of 3–12 μm, purity ≥98 wt%, carboxyl content at about 0.5 mmol g$^{-1}$) was used in this work as the carbon support to prepare the ZrO$_2$/MWCNTs composites. ZrOCl$_2$·8H$_2$O (99 wt%) purchased from Aladdin Reagent Co. Ltd. (Shanghai, China) was used as the Zr precursor for the synthesis. Surfactant polyvinyl pyrrolidone (PVP, average molecular 58,000) supplied by Macklin Biochemical Co., Ltd. (Shanghai, China) was used to improve the dispersibility of carbon nanotubes in solution.

In the activity test of catalysis, chemicals including fructose (≥99 wt%), 5-hydroxymethyl-2-furfural (5-HMF, 99 wt%), and levulinic acid (LA, 99 wt%) were purchased from Aladdin Reagent Co. Ltd. (Shanghai, China). Dimethyl silicone oil (500 cSt, 25 °C as the heat transfer fluid) and dimethyl sulfoxide (DMSO, >99.80 wt% as the solvent) were purchased from Heowns Biochemical Technology Co., Ltd. (Tianjin, China).

2.2. Synthesis of ZrO$_2$/MWCNTs(C) composites

A typical procedure for preparing the supported ZrO$_2$ on carbon materials under MW irradiation is described below (using MWCNTs(C) as the carbon support). Firstly, MWCNTs(C) powder (0.3 g) was dispersed in 60 mL deionized water with PVP via and ultrasonic treatment for 120 min at room temperature to homogenize the system. Then ZrOCl$_2$·8H$_2$O (1.176 g, corresponding to about 60 wt% loading) was added into the liquid mixture via ultrasonic treatment for another 30 min. Then the black suspension was placed in a multimodal microwave reactor and heated for 8 min (at 700 W, the equipment of the MW synthesis system was shown in Fig. S1). After the synthesis, the system was cooled to room temperature and centrifuged to separate solids in the system. Then the solids were washed several times using ethanol and dried at 70 °C under vacuum for 12 h. The synthetic time was varied in a range of 5–120 min to investigate its effect on the resulting composites. Unsupported bulk ZrO$_2$ was also synthesized with the same MW procedure. The conventional hydrothermal synthesis method based on the previous work [22] was used to prepare ZrO$_2$/MWCNTs composites as the control group catalysts. The catalyst for conventional hydrothermal synthesis was synthesized in stainless steel Teflon-lined autoclave reactor (100 mL capacity, at 180 °C for 720 min). For better differentiation, the obtained composites were named as CH/MW-ZrO$_2$/MWCNTs(C)-α, in which CH and MW represent the conventional and microwave synthesis method, respectively. $\alpha$ refers to the synthesis time (in min), and the bulk ZrO$_2$ was named as MW-ZrO$_2$-8.

2.3. Characterization of materials

Comprehensive characterization of the materials under investigation was achieved by a combination of techniques, including X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), Fourier transform infrared (FTIR), pyridine adsorption Fourier-transform infrared (Py-IR), nitrogen (N$_2$) physisorption and inductively coupled plasma optical emission spectrometry (ICP-OES). The details of the characterization techniques are described
in the part one of Supplementary Information (SI). In order to quantify the MW-absorbing ability of materials, the network analyzer (Keysight, ENA-85033C) equipped with a coaxial probe was used to measure the dielectric constant and loss of the carbonaceous materials (at 2.45 GHz) [33].

2.4. Catalytic fructose conversion

Catalytic fructose dehydration to 5-HMF was carried out in a laboratory batch reactor under conventional heating conditions, and the experimental set-up was shown in Fig. S2. In a typical experiment, 0.2 g of catalyst was added into the reactor with 20 mL DMSO and treated by sonication for 5 min to ensure homogenization of the suspension. After that, the mixture was heated to 120 °C, and then 0.5 g of fructose was charged into the reactor to initiate the reaction. The reaction was performed at 120 °C for 5 min. Afterwards, the reactor was rapidly quenched by immersing it into an ice-water bath. Next, the catalyst was separated from reactants by centrifugation. The liquid sample was quenched by immersing it into an ice-water bath. The original sample was washed with water and dried at 100 °C for 4 h.

3. Results and discussion

3.1. Material characterization

Generally, the conventional hydrothermal synthesis with CNTs as the support requires a reaction at 180 °C for 12 h to obtain ZrO$_2$/CNTs composite catalysts [34]. In this work, zirconia structure was grown on the surface of MWCNTs(C) successfully regardless of MW or CH hydrothermal conditions. Under the MW conditions, as shown in Fig.S3, a perfect ZrO$_2$/MWCNTs composite catalyst can be prepared in only 8 min, and the particle size of zirconia on MWCNTs gradually increases with the synthetic time. Comprehensive XRD and FTIR characterization of the materials were performed. As shown in Fig. 1a, by comparing MWCNTs(C) support with the physical mixture of zirconia/MWCNTs (C), the broad hump located at 26.1° can be assigned to the (002) reflections of the graphite phase of MWCNTs(C) [35]. The ZrO$_2$ scattering hump of the catalyst prepared by the MW hydrothermal (MW-ZrO$_2$/MWCNTs(C)-8) was not observed compared to that of the catalyst prepared by the conventional hydrothermal synthesis (i.e., CH-ZrO$_2$/MWCNTs(C)-720), which could be due to the larger ZrO$_2$ particles formed by conventional hydrothermal method. In the diffraction pattern of CH-ZrO$_2$/MWCNTs(C)-720, peaks located at 24.4, 28.2°, 31.5°, and 30.2°, 35.1°, 50.3° belong to the monoclinic crystalline ZrO$_2$ (m-ZrO$_2$) [36] and tetragonal ZrO$_2$ (t-ZrO$_2$) phases [37], respectively, showing that crystalline ZrO$_2$ was successfully supported on the MWCNTs(C) under conventional hydrothermal synthesis. Conversely, these diffraction peaks of ZrO$_2$ phases were not identified in MW-ZrO$_2$/MWCNTs(C)-8, suggesting the presence of highly dispersed ZrO$_2$ with small particle size on MWCNTs(C). However, it is also worth noting that amorphous ZrO$_2$ has a broad halo hump at around 20–40° [38–41], which overlaps with that of MWCNTs(C). Comparing the diffraction patterns of the bulk ZrO$_2$ with MW-ZrO$_2$ shows that the bulk ZrO$_2$ synthesized by the MW method was amorphous, which suggested that the supported ZrO$_2$ in the MW-ZrO$_2$/MWCNTs(C)-8 could be amorphous. Fig. 1b shows the FTIR spectra of relevant materials under study. The absorption band centered at 2930 cm$^{-1}$ is assigned to the $\nu$-OH groups stretching vibration from the carbon support [42]. The band at about 400–750 cm$^{-1}$ identified in CH-ZrO$_2$/MWCNTs(C)-720 is associated with vibration modes of Zr–O [43,44]. In detail, the peak at ~492 cm$^{-1}$ and ~755 cm$^{-1}$ can be attributed to the tetragonal and monoclinic phases of ZrO$_2$, respectively [45]. However, these FTIR peaks related to crystalline ZrO$_2$ were not detected in MW-ZrO$_2$/MWCNTs(C)-8. Therefore, the findings by FTIR agree well with that of XRD analysis, suggesting the presence of amorphous ZrO$_2$ in the composite prepared by the MW synthesis.

In order to further investigate the surface composition of the synthesized materials, XPS measurement was carried out, and the results were presented in Fig. 2. As shown in Fig. 2a, the XPS survey scans of the materials show the presence of elemental peaks of O 1 s, Zr 3 s, Zr 3p, Zr 3d in the two composites, which confirms the formation of ZrO$_2$/MWCNTs(C). Comparing the XPS spectra of MW-ZrO$_2$/MWCNTs(C)-720 and the peak intensity of C at 284.6 eV in MWCNTs(C) decreases 30.2°, 35.1°, 50.3°, suggesting the presence of highly dispersed ZrO$_2$ in the composite prepared by the MW synthesis.

In order to further investigate the surface composition of the synthesized materials, XPS measurement was carried out, and the results were presented in Fig. 2. As shown in Fig. 2a, the XPS survey scans of the materials show the presence of elemental peaks of O 1 s, Zr 3 s, Zr 3p, and Zr 3d in the two composites, which confirms the formation of ZrO$_2$ phases on the surface of MWCNTs(C) after the CH and MW hydrothermal synthesis. By comparing the XPS spectra of CH-ZrO$_2$/MWCNTs(C)-720 and MWCNTs(C), the Zr 3d peaks appear in CH-ZrO$_2$/MWCNTs(C)-720 and the peak intensity of C at 284.6 eV in MWCNTs(C) decreases greatly as well as the peak intensity of O increases sharply, suggesting that the MWCNTs(C) was coated by ZrO$_2$ phase after the MW hydrothermal synthesis [20]. However, the intensity of Zr and O in the XPS spectra of MW-ZrO$_2$/MWCNTs(C)-8 is significantly weaker than that of CH-ZrO$_2$/MWCNTs(C)-720, suggesting that the relatively low loading of ZrO$_2$ in the composites prepared by the MW hydrothermal synthesis.

![Fig. 1. (a) XRD patterns of ZrO$_2$/MWCNTs(C) composites, MWCNTs(C), ZrO$_2$ and MWCNTs(C)/ZrO$_2$ mixture (MWCNTs(C) + ZrO$_2$) and (b) FTIR spectra of MWCNTs(C) and ZrO$_2$/MWCNTs(C) composites prepared under MW and hydrothermal conditions.](image-url)
Fig. 2 b and c show that the peak protrusions at 291.5 and 533.9 eV represent the carboxyl groups on the MWCNTs(C). Notably, they are less obvious in the spectra of the composites, which implies the possible formation of Zr–O bonds during the synthesis process between Zr precursor and the surface hydroxyl/carboxyl groups of MWCNTs(C). As shown in Fig. 2 d, the twin peaks of Zr 3d with the binding energies at 182.9 and 185.3 eV correspond to the Zr 3d$_{3/2}$ and Zr 3d$_{5/2}$ chemical states, respectively, suggesting the +4 oxidation states Zr and the presence of Zr–O bonds [46]. It also indicates that the zirconia on the support is chemically bonded to the MWCNTs rather than simply physically adsorbed, which can enhance the stability of the composite in catalysis. Ordinarily, ZrO$_2$ peaks should be located at 182.6 and 185.1 eV. Here, the shift of the ZrO$_2$ characteristic peak may be due to the electron-withdrawing action of MWCNTs(C) at the binding site [47].

The peaks at 183.2 and 185.9 eV in MW-ZrO$_2$/MWCNTs(C)-8 can be assigned to Zr$^{\delta+}$, whose binding energy is between Zr$^{3+}$ and Zr$^{4+}$. Based on the investigation, Zr$^{\delta+}$ corresponds to a new chemical state, in which Zr–O bonds are more covalent than that of ZrO$_2$ [48]. The formation of the unique Zr structure can be due to the selective heating and "hot spots" formation on MWCNTs(C) under MW irradiation [49, 50]. In summary, according to XPS characterization, both the conventional and MW hydrothermal synthesis can prepare the supported ZrO$_2$ on MWCNTs(C), but the chemical state and loading of the ZrO$_2$ phases prepared by the two methods are rather different.

The composites (of CH-ZrO$_2$/MWCNTs(C)-720 and MW-ZrO$_2$/MWCNTs(C)-8) were further characterized by TEM and HRTEM to understand their physicochemical properties. Fig. 3 a–c show that large ZrO$_2$ particles were formed on MWCNTs(C) of CH-ZrO$_2$/MWCNTs(C)-720 after the conventional hydrothermal synthesis. Moreover, the ZrO$_2$ particles on MWCNTs(C) were unevenly distributed and aggregated, which agreed with the previous reports [20]. As shown in Fig. 3 d, the particle size distribution (PSD) of the loaded ZrO$_2$ particles was obtained based on the TEM analysis of the CH-ZrO$_2$/MWCNTs(C)-720, and the median particle size was about 35 nm. Moreover, the dark-field TEM and EDS mapping of CH-ZrO$_2$/MWCNTs(C)-720 also show the formation of large ZrO$_2$ around MWCNTs(C), as shown in Fig. 3 e, and it could be due to the preferred nucleation of Zr phases on the surface carboxyl groups on MWCNTs(C). Comparatively, after the 8-min MW synthesis, the resulting supported ZrO$_2$ particles can hardly be seen in the bright-field TEM images of Fig. 3 f and g, as well as in the HRTEM micrograph of Fig. 3 h. ZrO$_2$ particles in MW-ZrO$_2$/MWCNTs(C)-8 were identified in the Dark-field mode of TEM and EDS, as shown in Fig. 3 j, to show the highly and uniformly dispersed ZrO$_2$ on the surface of MWCNTs(C) with a narrower PSD centered at about 4.5 nm (Fig. 3 i). This was further proved by EDS mapping analysis of MW-ZrO$_2$/MWCNTs(C)-8 (Fig. 3 j), in which the presence of Zr, C, and O species with good dispersion on MWCNTs(C) was confirmed, validating that ZrO$_2$ nanoparticles were grown on MWCNTs(C) successfully after the 8-min MW synthesis. In addition, as shown in Figs. 3 h and SS, crystal lattice was not observed for the supported ZrO$_2$ on MWCNTs(C) under MW synthesis, which
suggested that amorphous ZrO$_2$ was prepared by the MW method and in line with the findings by XRD and FTIR.

To conclude, in comparison with the conventional hydrothermal synthesis, the supported ZrO$_2$ particles synthesized by the MW method have smaller and more uniform particle sizes on the surface of MWCNTs (C). Importantly, in the conventional hydrothermal synthesis, extended synthesis time (e.g. 720 min) was needed to enable the growth of ZrO$_2$ on MWCNTs(C) with large particles (Fig. S4), while in the MW synthesis, only 8 min was enough for preparing the well-dispersed ZrO$_2$ nanoparticles on MWCNTs(C). Meanwhile, the supported ZrO$_2$ prepared by the MW synthesis presents a unique amorphous structure, which is different from the tetragonal and monoclinic ZrO$_2$ phases prepared by the conventional hydrothermal synthesis. Interestingly, we found that the composite (MW-ZrO$_2$/MWCNTs-8) can still be synthesized by the MW method even with uncarboxylated MWCNTs, seen in Fig. S6 in SI. A possible explanation is that surface carboxyl groups are no longer necessary to provide nucleation sites for ZrO$_2$ growth under the MW conditions due to the selective heating of MWCNTs(C), while the high local temperature of the support promotes the growth of ZrO$_2$ on MWCNTs(C).

TGA and DSC analyses of MWCNTs(C), MW-ZrO$_2$/MWCNTs(C)-8 and CH-ZrO$_2$/MWCNTs(C)-720 suggested the nature of the supported ZrO$_2$ prepared by the two synthesis methods. As shown in Fig. 4, both MW-ZrO$_2$/MWCNTs(C)-8 and CH-ZrO$_2$/MWCNTs(C)-720 show the exothermic peak at about 350 $^\circ$C, and the intensity of the exothermic peaks of CH-ZrO$_2$/MWCNTs(C)-720 is significantly smaller than that of MW-ZrO$_2$/MWCNTs(C)-8. According to the literature [39], the exothermic peak at ~350 $^\circ$C corresponds to the ZrO$_2$ phase change, transforming from amorphous ZrO$_2$ to the tetragonal phase. Furthermore, the intensity of the exothermic peak of MW-ZrO$_2$/MWCNTs(C)-8 at ~350 $^\circ$C is significantly stronger than that of CH-ZrO$_2$/MWCNTs(C)-720, indicating that the amorphous ZrO$_2$ is dominant in MW-ZrO$_2$/MWCNTs(C)-8. In contrast, the crystalline zirconia is common in the composite of CH-ZrO$_2$/MWCNTs(C)-720 from the conventional hydrothermal synthesis.

The residual mass of CH-ZrO$_2$/MWCNTs(C)-720 after TGA (at 900 $^\circ$C) is about 36%, which is almost 2.5 times higher than that of MW-ZrO$_2$/MWCNTs(C)-8 (~13%), indicating that the loading amount of

Fig. 3. (a), (b) TEM, (c) HRTEM, (d) particle size distribution (PSD), and (e) EDS mapping of CH-ZrO$_2$/MWCNTs(C)-720; (f), (g) TEM, (h) HRTEM, (i) PSD, and (j) EDS mapping of MW-ZrO$_2$/MWCNTs(C)-8.

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ZrO₂ in CH-ZrO₂/MWCNTs(C)-720 is much more than that of in MW-ZrO₂/MWCNTs(C)-8. The findings by TGA and DSC agree well with the results of TEM and XRD, which support the discussion on the crystalline structure of the composites prepared by different synthesis methods.

Pyridine FT-IR spectroscopy was used to characterize the nature and amount of acid sites on the composite surface, as shown in Fig. S7 and Table 1. The absorption peaks located at around 1451, 1490 and 1610 cm⁻¹ can be assigned to Lewis acid sites, and the absorption peak located at 1540 cm⁻¹ is attributed to Brønsted acid sites [45]. Based on the methods reported previously [51,52], surface concentrations of Lewis and Brønsted acid sites were calculated as shown in Table 1, showing that CH-ZrO₂/MWCNTs(C)-720 possesses more surface acidic sites than MW-ZrO₂/MWCNTs(C)-8. While the number of acidic sites of the bulk MW-ZrO₂-8 is between them.

ICP-OES measured the actual Zr content in the three materials of MW-ZrO₂-8, CH-ZrO₂/MWCNTs(C)-720, and MW-ZrO₂/MWCNTs(C)-8 (expressed as Zr wt%), and the results are presented in Table 1. Based on the measured data, the bulk MW-ZrO₂-8, the atomic ratio of Zr to O is close to 1:2, indicating that it basically contains no impurities. CH-ZrO₂/MWCNTs(C)-720 prepared by the conventional hydrothermal synthesis possesses higher ZrO₂ loading than MW-ZrO₂/MWCNTs(C)-8. Accordingly, the relatively low acidity of MW-ZrO₂/MWCNTs(C)-8 can be explained by the comparatively low Zr loading on MWCNTs(C) in comparison with that of CH-ZrO₂/MWCNTs(C)-720.

Textural properties of the MWCNTs(C) support and the CH-ZrO₂/MWCNTs(C)-720 and MW-ZrO₂/MWCNTs(C)-8 composite were assessed using N₂ physisorption, and the results are shown in Fig. S8. Nitrogen porosimetry revealed that MWCNTs(C) and the composite based it has the isotherms similar to the type II one, which is basically non-porous, as evidenced by the insignificant rise in the amount adsorbed at low relative pressures. The specific Brunauer-Emmett-Teller (BET) surface area and total pore volume (at P/P₀ = 0.99) of the pristine MWCNTs(C) support were measured as 416 m²·g⁻¹ and 1.79 cm³·g⁻¹, respectively, which was likely due to the packing of the internal space of MWCNTs(C). After the loading of ZrO₂, the BET surface area, as well as the pore volume of the CH-ZrO₂/MWCNTs(C)-720 and MW-ZrO₂/MWCNTs(C)-8 catalysts, dropped significantly, which could be the result of channel blockage and/or surface coverage (of MWCNTs(C)) caused by the low surface area ZrO₂ phase [53]. In addition, CH-ZrO₂/MWCNTs(C)-720 presented a smaller BET surface area of 164 m²·g⁻¹ and a lower pore volume of 0.70 cm³·g⁻¹ in comparison with that of MW-ZrO₂/MWCNTs(C) (192 m²·g⁻¹ and 0.74 cm³·g⁻¹, respectively), which suggests that MW-ZrO₂/MWCNTs(C)-8 has a lower zirconia loading.

### 3.2. Mechanisms of ZrO₂ deposition on MWCNTs(C)

Based on the above characterization measurements, highly dispersed amorphous ZrO₂ was successfully deposited on the surface of MWCNTs(C) after the MW synthesis (8 min). Conversely, large crystalline ZrO₂ particles were synthesized on MWCNTs(C) via the time-consuming conventional hydrothermal route (720 min). In order to explain the difference in the ZrO₂ phases resulting from the two synthesis methods, the following mechanisms were proposed, as shown in Fig. 5.

According to previous research [20,54], the reaction paths can be described as Eq. (1) and Eq. (2) that the hydrolysis of ZrOCl₂ occurs in an aqueous system, which forms Zr(OH)₄ and HCl. With the increase of system temperature, the volatilization of HCl breaks the reaction equilibrium of Eq. (1), leading to the increase of the concentration of Zr(OH)₄ that is adsorbed by the MWCNTs(C). Condensation of the adsorbed Zr(OH)₄ leads to the formation of the supported ZrO₂ on MWCNTs(C).

### Table 1

| Sample                      | Total acidity (μmol·g⁻¹) | Brønsted acid amount (μmol·g⁻¹) | Lewis acid amount (μmol·g⁻¹) | Brønsted/Lewis | Zr content (%) |
|-----------------------------|-------------------------|--------------------------------|----------------------------|----------------|----------------|
| CH-ZrO₂/MWCNTs(C)-720      | 61.91                   | 5.44                           | 56.07                      | 0.966          | 42.79          |
| MW-ZrO₂/MWCNTs(C)-8        | 47.09                   | 3.04                           | 44.04                      | 0.069          | 6.31           |
| MW-ZrO₂-8                  | 85.22                   | 2.98                           | 82.24                      | 0.036          | 73.32          |

**Fig. 4.** TGA and DSC analysis of MWCNTs(C), MW-ZrO₂/MWCNTs(C)-8 and CH-ZrO₂/MWCNTs(C)-720.
ZrOCl₂ + 3H₂O → Zr(OH)₄ + 2HCl \hspace{1cm} (1)
Zr(OH)₄ → ZrO₂ + 2H₂O \hspace{1cm} (2)

When Zr(OH)₄ is formed in the liquid bulk, it tends to interact with the surface carboxyl group via electrostatic adsorption [54]. Accordingly, the past study employing MWCNTs requires the pretreatment of the carbon support (via oxidation) to generate sufficient functional groups on the surface of MWCNTs as nucleation sites to facilitate ZrO₂ growth (via Zr(OH)₄ condensation) under hydrostatic conditions [54]. ZrOCl₂ could interact with surface –COOH directly via esterification to form the C–O–Zr bond on the surface of MWCNTs and subsequently form ZrO₂ under the conventional hydrothermal synthesis [14,20]. Nevertheless, under the conventional hydrothermal conditions, the presence of O-containing surface groups on MWCNTs is key to the deposition of ZrO₂. As a result, an increase in the size of the deposited ZrO₂ can be expected by extending the synthesis time in these conventional syntheses. In hydrothermal synthesis, the crystalline property of the deposited ZrO₂ is mainly related to the pH value and reaction temperature of the system. Gao et al. showed that high temperatures (150 °C) and acidic conditions (pH < 3) could promote the formation of tetragonal ZrO₂ on MWCNTs [29]. Conversely, the monoclinic zirconia nanoparticles supported on MWCNTs were synthetized under low-temperature conditions. Compared to monoclinic ZrO₂, tetragonal ZrO₂ benefits the catalytic properties due to a relatively strong acidity [55,56]. Therefore, the growth mechanism of the supported ZrO₂ on MWCNTs(C) (i.e., CH-ZrO₂/MWCNTs(C)-720) under the hydrothermal condition is well supported by previous studies, which includes the nucleation of Zr precursors on the surface -COOH, followed by the formation of crystalline monoclinic/tetragonal phases on MWCNTs(C), as shown by the mechanism above in Fig. 5. Since the condition used in this work was 180 °C, the tetragonal phase was encouraged in CH-ZrO₂/MWCNTs(C)-720.

Under the MW condition, the rapid and selective heating of the MW absorbing carbon support (i.e. MWCNTs(C)) leads to quite different growth mechanisms of ZrO₂ on MWCNTs(C) from that under the conventional hydrothermal condition [46,57,58]. According to the theory of dielectric heating [49], the higher the dielectric constant and dielectric loss is, the higher the MW absorbing ability of the material is. Especially, MWCNTs(C) have a strong dielectric constant and dielectric loss than surrounding solvents (seen in Table S1), suggesting that the MWCNTs(C) would be selectively and rapidly heated under MW irradiation and generated microscopic “hot spots” over their surface [28]. Such a considerable temperature gradient makes it easier for Zr(OH)₄ in solution to undergo decomposition reaction on the superheated MWCNTs(C) surface to form ZrO₂ and uniformly deposit on the MWCNTs(C) surface [40]. While in the conventional hydrothermal synthesis, the MWCNTs(C) support and solution have the same temperature, and Zr(OH)₄ is more inclined to decompose in solution [54,59]. Therefore, different from MW hydrothermal synthesis, the surface carboxyl groups of MWCNTs are necessary to provide nucleation sites for the growth of ZrO₂ on the MWCNTs surface in conventional hydrothermal synthesis. In addition, it was also reported that MW irradiation could promote the nucleation and crystallization process of metal oxides such as Silicalite-1 and VSB-5 molecular sieves, and the effect appears to be much more apparent on the nucleation step relative to crystal growth [60]. Consequently, the deposition of ZrO₂ on the MWCNTs(C) under microwave irradiation would not depend on the surface carboxyl groups. With the strong MW-absorbing MWCNTs(C), ZrO₂ was directly deposited on its surface due to the local hot surface under MW irradiation. Since converting the Zr precursor to ZrO₂ is rather quick, the formed ZrO₂ is amorphous rather than crystalline (as evidenced by XRD and TEM analysis above). A similar phenomenon of forming smaller particles and the amorphous phase of bulk ZrO₂ under MW irradiation was also reported previously [40], while the formation of local “hot spots” on MW-absorbing materials under MW irradiation was directly observed in the previous study [28]. Based on the above analysis, the synthesized catalyst was almost inactive without the carboxyl group on the MWCNTs in the conventional hydrothermal synthesis. With the surface groups in the case of MWCNTs(C), ZrO₂ gradually grew into aggregates at the nucleation sites (of carboxyl groups) with an increase in synthesis time, as proposed in Fig. 5. In the MW method, unlike the conventional hydrothermal method, the nucleation of ZrO₂ on the MWCNTs(C) surface under MW irradiation could be no longer dependent on the adsorption sites of carboxyl groups on the support, i.e., direct deposition of ZrO₂ phase on MWCNTs(C) in the MW synthesis was likely.

In summary, in the conventional hydrothermal synthesis, ZrO₂ growth was preferred with the surface –COOH and gradually formed large ZrO₂ particles on MWCNTs(C) with an extended synthesis time, which was also reported previously [60]. However, the aggregation of the ZrO₂ phase on MWCNTs(C) reduces the availability of the relevant
reactive sites on the carbon support, resulting in a relatively low catalyst activity (to be discussed later). Conversely, in the MW synthesis, the strong absorption of MW by MWCNTs(C) creates local “hot spots” on their surface, which enable the formation of highly dispersed and small ZrO₂ particles to increase the effective contact area between the reactants and the catalyst [14,30]. In addition, the amorphous structure could be more beneficial in the catalytic conversion of fructose than the monoclinic and tetragonal phases [49], which will be discussed below.

3.3. Catalytic conversion of fructose to 5-HMF over the composite catalysts

The developed ZrO₂/MWCNTs(C) composite catalysts and the control catalysts were assessed in the model reaction of catalytic fructose conversion to 5-HMF to investigate their activity. Under the same catalytic condition (i.e., 0.5 g fructose with 0.2 g catalyst under 20 mL DMSO at 120 °C bulk system temperature and atmospheric pressure), the catalytic performance of the MW-ZrO₂-8 (bulk), MW-ZrO₂/MWCNTs(C)-8 and CH-ZrO₂/MWCNTs(C)-720 catalyst were obtained and presented in Fig. 6. It was found that, under the reaction condition used, dehydration of fructose could proceed over all the catalysts. Comparatively, the CH-ZrO₂/MWCNTs(C)-8 catalyst was the least active one compared to the MW-ZrO₂/MWCNTs(C)-8 and bulk MW-ZrO₂-8. In detail, a fructose conversion of 24.8% and a 5-HMF yield of 15.7% were achieved by CH-ZrO₂/MWCNTs(C)-720 after a 5-min reaction. While MW-ZrO₂/MWCNTs(C)-8 achieved 72.8% and 63.0%, and the bulk MW-ZrO₂-8 achieved 53.25% and 41.27%, respectively. For the reaction catalyzed over CH-ZrO₂/MWCNTs(C)-720 and MW-ZrO₂-8, the catalytic system could reach the steady-state after 60 min on stream. Conversely, over MW-ZrO₂/MWCNTs(C)-8, steady-state was quickly established in 20 min, leading to a 5-HMF yield of 86.1%, which suggests that MW-ZrO₂/MWCNTs(C)-8 can improve the reaction kinetics significantly in comparison with CH-ZrO₂/MWCNTs(C)-720. As shown in Table S2, carbon balance of the catalytic reactions are above 92%.

The effect of the bulk system temperature and catalyst loading on the performance of MW-ZrO₂-8/MWCNT(C)-8 for catalyzing fructose conversion was studied, and the results were shown in Fig. S9. The bulk system temperature affected fructose conversion and 5-HMF yield positively. In the presence of the MW-ZrO₂/MWCNT(C)-8 catalyst, fructose conversion increased with an increase in catalyst amount, with the maximum 5-HMF yield of about 63% in the case of 0.2 g MW-ZrO₂/MWCNT(C)-8 with 0.5 g fructose (i.e., 40 wt%). However, a further increase of the catalyst loading from 40 wt% caused the decrease in 5-HMF yield due to the production of by-products, as evidenced by Fig. S10 and Table S3.

The acidity of the catalyst could play a vital role, especially in the catalytic conversion of sugars into 5-HMF, and Bronsted acid sites promoted the dehydration of fructose to form HMF [61]. Turnover frequency (TOF) was calculated from the rate of produced 5-HMF (5 min) and acid site concentration (Bronsted acid sites) [62], as listed in Table 2. This reaction rate of MW-ZrO₂/MWCNTs(C)-8 was nearly four times that of CH-ZrO₂/MWCNT(C)-720, and the TOF of MW-ZrO₂/MWCNTs(C)-8 was more than seven times that of CH-ZrO₂/MWCNTs(C)-720. MW-ZrO₂/MWCNTs(C)-8 showed the highest catalytic activity despite the low acidity, indicating that the amorphous ZrO₂ structure enhanced the reaction rate. According to the catalytic and characterization data of the catalysts, the particle size and degree of aggregation of the supported ZrO₂ could be important factors to affect the catalytic activity in the selective conversion of fructose to 5-HMF. Regarding CH-ZrO₂/MWCNTs(C)-720, although its crystallinity and acidity are high

| Sample | Rate of 5-HMF production (mmol L⁻¹ min⁻¹) | TOF (min⁻¹) |
|--------|------------------------------------------|-------------|
| CH-ZrO₂/MWCNTs(C)-720 | 4.7 | 80.1 |
| MW-ZrO₂/MWCNTs(C)-8 | 17.5 | 574.9 |
| MW-ZrO₂-8 | 11.5 | 384.4 |

Table 2. Catalytic activity of MW-ZrO₂-8, CH-ZrO₂/MWCNTs(C)-720 and MW-ZrO₂/MWCNTs(C)-8.

\(a\) Reaction conditions: 0.5 g fructose, 0.2 g catalyst, 20 mL DMSO, at 120 °C and atmospheric pressure for 5 min.

\(b\) TOF was estimated from the initial rate per Bronsted acid sites [62].
(compared to that of MW-ZrO$_2$/MWCNTs(C)-8), its catalytic activity was relatively poor, which could be due to severe aggregation of the deposited ZrO$_2$ on MWCNTs(C), limiting the available active sites for catalysis. Conversely, for MW-ZrO$_2$/MWCNTs(C)-8, the highly dispersed amorphous ZrO$_2$ with smaller particle sizes showed a better catalytic activity, suggesting that crystallinity might not be the key for explaining the catalytic activity of the supported in ZrO$_2$ catalysis.

In order to assess the performance of the developed MW-ZrO$_2$/MWCNTs(C)-8 catalyst, a comparison with state of the art regarding fructose dehydration and 5-HMF yield was carried out (Table S4 and Table S5). Compared to the studies employing metal oxides, zeolites, ion exchange resin and sulfonated carbons, the MW-ZrO$_2$/MWCNTs(C)-8 catalyst shows excellent catalytic activity in catalytic fructose conversion, whilst showing the performance of CH-ZrO$_2$/MWCNTs(C)-720 is relatively low. Hence, the advantage of the highly dispersed amorphous ZrO$_2$ the MW-ZrO$_2$/MWCNTs(C)-8 catalyst, which was synthesized by the efficient MW synthesis, is highlighted.

Regarding the recyclability of MW-ZrO$_2$/MWCNTs(C)-8 and CH-ZrO$_2$/MWCNTs(C)-720, experimental results (Fig. S11) show that both of them has good cycling stability. 5-HMF yield over CH-ZrO$_2$/MWCNTs(C)-720 decreased with an increase in the number of stability cycles, and the difference in the 5-HMF yield for the initial and final cycle was approximately 5%. Deactivation of MW-ZrO$_2$/MWCNTs(C)-8 was also measured, regarding 5-HMF yield over MW-ZrO$_2$/MWCNTs(C)-8, it dropped by ~12.5% (from 62.9% to 50.4%) at the end of the stability test. Deactivation of the composite catalysts might be due to the coke deposition on the active sites and/or leaching of the ZrO$_2$ nanoparticles, as shown in Table S6 and Fig. S7. However, TEM analysis of the used catalysts (after 5 recycles, Fig. S12) showed no apparent changes of size and original superstructure in comparison with the fresh ones, indicating a stable catalyst structure.

Additionally, it was also found that under the MW condition, the particle size of the supported ZrO$_2$ could be increased by prolonging the synthesis time, as shown in Fig. S13. However, the increase in ZrO$_2$ particle sizes was not beneficial to the 5-HMF yield in fructose conversion. At the same time, it was also found that during the MW synthesis surface -COOH group was not the prerequisite for enabling the growth of ZrO$_2$. Conversely, the dielectric constant and dielectric loss of the carbon supports played a role in the process, as shown in Table S1, which affected their catalytic efficiency in the selective conversion of fructose to 5-HMF. Experiment for higher initial zirconia concentration was also conducted, the physiochemical properties of the MW-synthesized ZrO$_2$/MWCNTs(C) composite (i.e., MW-ZrO$_2$/MWCNTs(C)-8) were revealed. In detail, highly dispersed amorphous ZrO$_2$ with very small particle sizes (about 4.5 nm) was found in MW-ZrO$_2$/MWCNTs(C)-8. Conversely, the conventional method promoted the large aggregation of crystalline ZrO$_2$ on MWCNTs(C) (i.e. in CH-ZrO$_2$/MWCNTs(C)-720). Such difference was attributed to the selective and rapid heating of the strong MW-absorbing support of MWCNTs(C) under MW irradiation, leading to the formation of microscopic ‘hot spots’ and therefore resulting in the rapid deposition of amorphous ZrO$_2$ nanoparticles on the surface of MWCNTs(C). More importantly, the developed MW method did not depend on surface carboxyl groups of the carbon support, while carboxyl groups were demanded under the conventional hydrothermal condition for nucleation of Zr species for crystal growth.

The composite materials under investigation were assessed in catalytic fructose conversion (to 5-HMF). MW-ZrO$_2$/MWCNTs(C)-8 showed a better catalytic performance than that of CH-ZrO$_2$/MWCNTs(C)-720 (which was prepared by the conventional hydrothermal synthesis) and MW-ZrO$_2$-8 (the unsupported bulk ZrO$_2$ prepared by the MW method) regarding fructose conversion and 5-HMF yield. For example, MW-ZrO$_2$/MWCNTs(C)-8 achieved 72.8% fructose conversion and 63.0% 5-HMF yield in 5 min, whilst CH-ZrO$_2$/MWCNTs(C)-720 only obtained 24.8% and 15.7%, respectively. The good catalytic performance of MW-ZrO$_2$/MWCNTs(C)-8 is related to its unique amorphous ZrO$_2$ phase supported on MWCNTs(C). In summary, the findings of the work shed light on the effectiveness of the MW-assisted synthesis, especially in combination with MW-absorbing materials, which can be further explored for other relevant systems requiring process intensification. For example, the employment of MW-responsive catalysts for process intensification of catalytic conversion of biomass and bio-derived chemicals under MW irradiation.

CRediT authorship contribution statement
Shiyun Mu: Conceptualization, Methodology, Formal analysis, Investigation, Writing – original draft. Kai Liu: Conceptualization, Methodology, Formal analysis, Investigation, Writing – original draft. Hong Li: Writing – review & editing, Project administration. Zhenyu Zhao: Methodology, Writing – review & editing. Xiaqi Lyu: Methodology. Yilai Jiao: Writing – review & editing, Formal analysis. Xingang Li: Resources. Xin Gao: Resources, Conceptualization, Formal analysis, Funding acquisition, Writing – review & editing, Supervision. Xiaolei Fan: Resources, Writing – review & editing, Formal analysis, Supervision.

Declaration 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.

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Appendix A. Supplementary data
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