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Carbon nanodot modified Cu-Mn-Ce/ZSM catalyst for enhanced microwave-assisted degradation of gaseous toluene

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Abstract:

In this work, carbon nanodots (CNDs) were firstly synthesized by hydrothermal treatment of natural biomass (dead leaves of plane tree) without any synthetic chemicals. The concentration of the fabricated carbon nanodot solution was *ca*. 13 g·L^{-1} and the mass yield of CNDs was *ca*. 5.6%. The characterization results indicated that the prepared CNDs with the sizes of 2-7 nm contained rich surface function groups such as O and N- containing groups and possessed blue fluorescence property. Using a conventional impregnation approach, the fabricated carbon nanodot solution was used to further modify Cu-Mn-Ce/ZSM (CMCZ) catalyst. The CNDs modified Cu-Mn-Ce/ZSM (CNDs-CMCZ) catalyst was subsequently evaluated by catalytic oxidation of gaseous toluene under microwave heating. The experimental results demonstrated that the modification of CNDs with the feature of analogous humic acids enhanced obviously the adsorptive capacity of gaseous toluene and the temperature-rising speed of catalyst during catalytic reaction compared to unmodified Cu-Mn-Ce/ZSM catalyst. The improved adsorptive capacity of gaseous toluene could be due to the enhanced specific surface area and the role of surface function groups of the composite catalyst, while the "hot spots" effect of the CNDs could significantly contribute the improved temperature-rising speed of the composite catalyst. Owing to these advantages, 75% of gaseous toluene was degraded within 80 min at 150 ℃ using CNDs-CMCZ catalyst, which was almost 1.9 times of that using unmodified catalyst. At lower reaction bed temperature (*e.g.*, 150 ℃), the obtained catalytic performance could be due to a synergistic role of carbon nanodots and Cu-Mn-Ce/ZSM. Although the degradation efficiency of gaseous toluene was further improved with increasing reaction bed temperature (200 ℃ and 250 ℃), the role of CNDs modification for improving catalytic performance was obviously weaken, which

could be ascribed to the structure and surface functional group damage of carbon nanodots at higher catalytic temperature. This work demonstrated the possibility of developing CNDs modified catalysts for low-temperature catalytic oxidation of volatile organic compounds (VOCs).

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1. Introduction

Because of many adverse factors to environment and human health after long exposure, toxic volatile organic compounds (VOCs) have aroused great attention in the fields of science and technology.[1-3] In recent years, many techniques have been developed to treat waste gas containing VOCs before they are able to be released to environment, such as adsorption,[4, 5] biological treatment,[6] and catalytic oxidation.[7] Among them, catalytic oxidation has become a popular technique to treat toxic and complex VOCs.[8, 9] As a core of catalytic oxidation technique, catalyst is critically important to achieve high treatment efficiency of VOCs. For this, many catalysts such as MnO_x/γ-alumina and $MnCuO_x$/TiO_2 catalysts have been developed to treat VOCs, exhibiting superior treatment performance.[10, 11] To further improve the treatment efficiency, coupling catalytic oxidation with other techniques such as microwave heating has also been widely explored for VOCs removal in many literatures.[12, 13] Microwave as an electromagnetic wave with high thermal effect, dipole polarization and versatile capacity, has been widely applied in environmental remediation.[14, 15] Microwave heating can importantly shorten the time of catalytic reaction bed temperature adjustment, thus improving catalytic treatment efficiency of VOCs.[16] In our previous studies, molecular sieve supported copper, manganese and cerium (Cu-Mn-Ce/ZSM) catalyst has been developed and evaluated in catalytic oxidation of VOCs under microwave heating assistance.[17] Our studies have demonstrated that the fabricated Cu-Mn-Ce/ZSM catalyst has strong microwave absorption capability, resulting in an effective removal of VOCs.[18] Even so, the conventional catalyst usually requires a higher catalytic reaction temperature

(350-600 °C) to generate more catalytic active sites on catalysts surface, which may be not unfavorable to large-scale application in VOCs treatment. Therefore, development of low-cost catalyst with high catalytic activity and low-temperature catalytic ability is highly desired.

J. A. Menéndez *et al.* have illustrated that biomass char possesses dual function as catalyst and microwave receptor in the process of catalytic oxidation reaction.[19] Based on this, carbon material modified catalysts have been widely investigated for removal of VOCs by coupling catalytic oxidation with microwave heating technique.[13, 20] Recently, carbon nanodots (CNDs) have attracted great research interest because of their abundant, benign, easy synthetic, inexpensive nature, rich surface function groups, and excellent fluorescence property.[21, 22] Owing to many superior properties, CNDs have been investigated in the areas of photocatalysis, photovoltaics, and fluorescent detection.[23] Due to the small sizes (<10 nm) and rich surface function groups, CNDs possess very different physical and chemical properties with the bulk carbon material.[24, 25] Especially, to the best of our knowledge, no reports have illustrated the effect of carbon nanodot modification on VOCs treatment efficiency of traditional catalyst under microwave heating.

Herein, we report a simple hydrothermal method to synthesize CNDs using dead leaves of plane tree as reaction precursor without any synthetic chemicals. The prepared CNDs were employed to further modify Cu-Mn-Ce/ZSM catalyst by a conventional impregnation approach. The resulting CNDs modified Cu-Mn-Ce/ZSM catalyst was evaluated by catalytic oxidation of gaseous toluene under microwave heating. For comparison, unmodified Cu-Mn-Ce/ZSM catalyst was also measured under the same experimental conditions.

2. Materials and methods

2.1 Preparation of carbon nanodots (CNDs)

CNDs sample was prepared by a simple hydrothermal approach similar with the reported methods.[23] In a typical process, dead leaves of plane tree were firstly collected from the campus of Xi'an university of architecture and technology (East longitude 107° 40'~ 109° 49' and north latitude 33° 39 '~ 34° 45'), and

then washed with deionized water and dried at 80 °C for 12 h for further use. Subsequently, 50 g dried leaves were directly put into 500 mL of deionized water, and then the mixture was transferred into a Teflon-lining autoclave and heated up to 180 °C for 3 h in an oven. After hydrothermal reaction, the autoclave was cooled to room temperature and the obtained product was centrifuged for 10 min at 12,000 r·min^{-1}, and CNDs solution with an excellent water solubility (pH = 4.16 ± 0.05) was collected for further use. The concentration of the fabricated CNDs solution is *ca*. 13 g·L^{-1} and the mass yield is about 5.6%.

2.2 Preparation of CNDs modified Cu-Mn-Ce/ZSM catalyst

Cu-Mn-Ce/ZSM catalyst was firstly prepared by conventional impregnation method as reported by Y. Zhang *et al.*.[26] The resulting Cu-Mn-Ce/ZSM catalyst was thermally treated at 400 °C for 4 h in a muffle furnace. The obtained Cu-Mn-Ce/ZSM catalyst was denoted as CMCZ with the spherical particle sizes of 3-4 mm. The calcined CMCZ (5.0 g) was then dispersed in 100 mL of diluted CNDs solution (10 mL of original CNDs solution was diluted to 100 mL using deionized water (pH = 7.04 ± 0.04)) for 6 h at 100 r·min^{-1} in a shaker. After that, the CNDs modified CMCZ was dried at 80 °C for 12 h in a vacuum oven. Through the above process, the loading amount of CNDs on CMCZ is about 19 mg·g^{-1}. The CNDs modified CMCZ was further expressed as CNDs-CMCZ.

2.3 Characterizations

The fluorescence property of the CNDs was recorded by a 3D-Spectrofluorometer (Jasco FP-6500) with fluorescence excitation–emission (Ex-Em) matrix (EEM) spectroscopy. The surface function groups of CNDs were measured on a Fourier transform infrared spectrometer (FT-IR, SHIMADZU IRPrestige-21). The composition of CNDs was further analyzed by X-ray photoelectron spectrometer (XPS, Thermo Scientific K-Alpha). The specific surface area and pore structure of the catalysts were recorded by a Specific Surface Area Analyzer (V-Sorb 2800P).

2.4 Catalytic oxidation of gaseous toluene under microwave heating

The catalytic oxidation of gaseous toluene was carried out in a fixed bed reactor under microwave

heating and continuous flow mode, where the quartz reactor with 30 mm inner diameter was vertically inserted in a microwave device and 110 g catalysts were installed prior to the experiment. The microwave device was a modified domestic microwave oven (2.45 GHz) with adjustable output power (max 700 W), which was controlled by a variable transformer.[27] In our experiment, gaseous toluene with initial concentration of 2000 mg·m^{-3} and flow rate of 0.08 m^3·h^{-1} was pumped into the reactor from the bottom under microwave irradiation, and relative gas hourly space velocity (GHSV) was 600 h^{-1}. The treated gas was purified by methanol and NaOH solutions in turns before discharged. Gaseous toluene concentrations in the inlet and outlet were collected and detected by gas chromatography (GC-FID, Aglient 6890N), and reaction bed temperature was measured by the thermocouple probe. For comparison, the experiment without microwave irradiation was also conducted under the same experimental conditions.

3. Results and discussion

3.1 Characteristics of CNDs

After diluting 10 mL of original CNDs solution into 200 mL, the obtained CNDs solution is yellow, and exhibits blue fluorescence under UV light (main wavelength of 365 nm) irradiation (photograph in Fig. 1A), which is in agreement with the reported results.[28] The UV-vis absorption spectra indicate that the absorption bands of the CNDs are located at around 270 nm (Fig. 1A), consistent with the reported results.[29] It has been reported that the excitation jump of electron-donating groups and discrete energy level structure of CNDs with the sizes of 1-10 nm can generate fluorescence easily under UV irradiation.[30] The above optical results indicated that the prepared CNDs possessed nanometer level size and electron-donating functional groups.[22] Transmission electron microscopy (TEM) analysis further confirms the CNDs with the sizes of 2-7 nm (Fig. 1B). Fig. 1C shows the excitation-emission matrix (EEM) spectrum of the CNDs. As shown, an outstanding isoheight peak (Ex/Em 325/450 nm) appears in the areas of excitation wavelength (300-360 nm) and emission wavelength (410-480 nm), indicating the CNDs with abundant analogous humic substances.[31, 32] The peak shown in Fig. 1C is uniform and proportional, which reveals the homogenization and

simplification of the species of humic substances,[33] further demonstrating the size uniformity of the fabricated CNDs in this work.
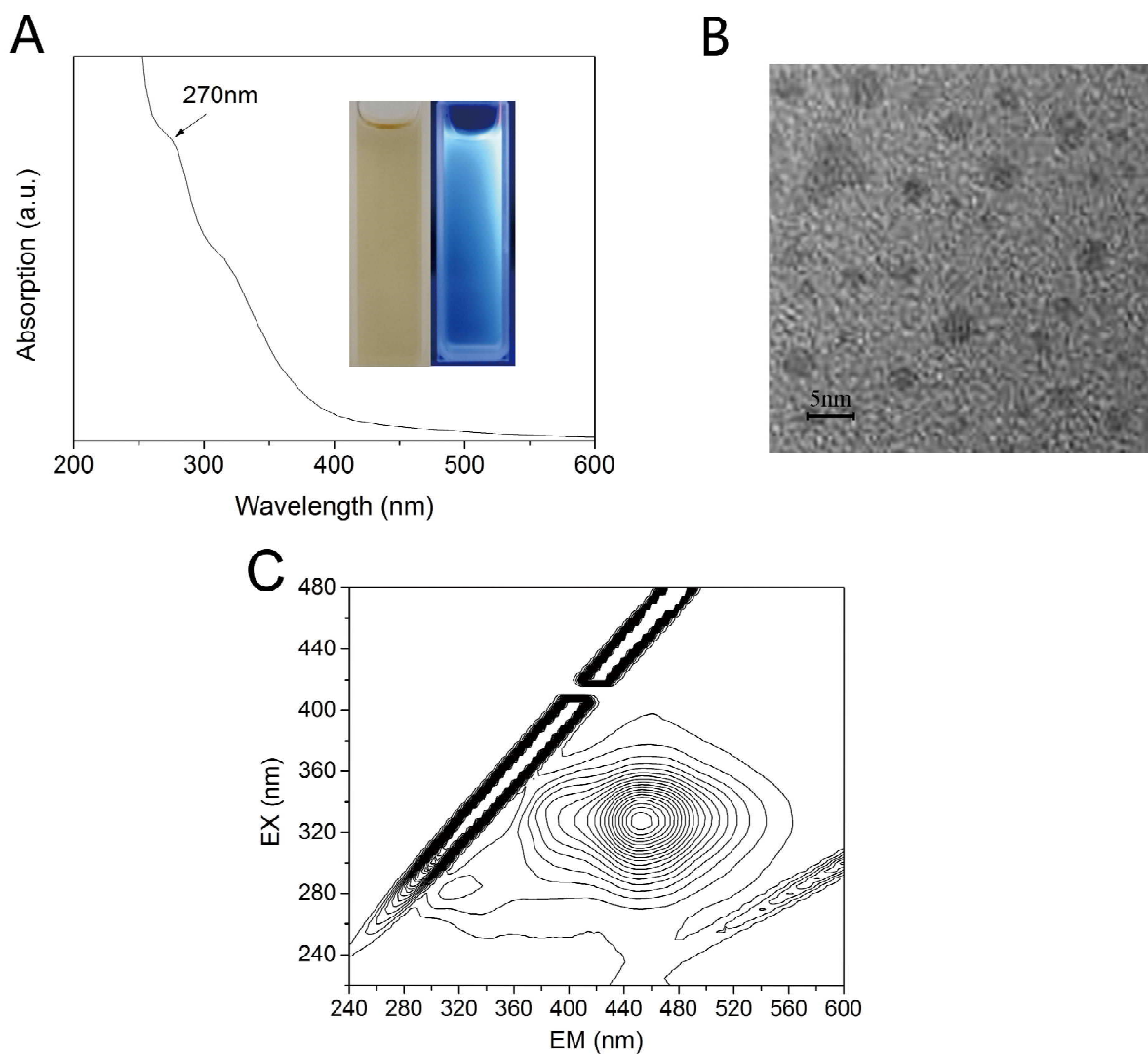

Fig. 1 (A) UV-Vis absorption spectrum and fluorescence photograph of the CNDs liquid compared with its original color. (B) Transmission electron microscopy (TEM) image of the CNDs. (C) Excitation–emission matrix (EEM) spectrum of the CNDs.

The surface function groups of the CNDs were analyzed by FT-IR technique and the corresponding spectra are shown in Fig. 2A. As shown, different absorption peaks can be observed in 3417 cm^{-1}, 2941 cm^{-1}, 1639 cm^{-1}, 1419 cm^{-1} and 1107 cm^{-1}, respectively, indicating the synthesized CNDs possesses complex surface function groups, which is in accordance with the reported results.[34-36] The peak of 2941 cm^{-1} was

regarded as the stretching vibration of C−H bond, and wide peak located at 3417 cm^{-1} could be the stretching vibration of O−H bond or N−H bond, and the peak centered at 1107 cm^{-1} could be stretching vibration of C−O bond or C−N bond.[37, 38] Therefore, carboxylic, phenolic and/or aminic function groups could be present in the CNDs.[39, 40] The peak located at 1639 cm^{-1} could be considered as the deformation vibration of N−H bond or stretching vibration of C=O bond, and the peak of 1419 cm^{-1} could be stretching vibration of C−N bond, so amide group could be also existed in the prepared CNDs. Moreover, it was found that some weak absorption peaks were appeared in the wavelengths between 1200 cm^{-1} and 1600 cm^{-1}, and these peaks verified that the CNDs could have the structure with aromatic ring, which was consistent with the fluorescence of the CNDs.[30, 41] Overall, the FT-IR results confirm that the fabricated CNDs possesses rich O and N-containing surface function groups, which may be beneficial for quick improving catalytic reaction temperature using the CNDs as microwave acceptor.[42] The surface function groups of the CNDs were further analyzed by X-ray photoelectron spectroscopy (XPS). The surface XPS survey spectra show that the CNDs is mainly composed of C, N and O (Fig. 2B), confirming the CNDs with nitrogen doping.[43] Fig. 2B further reveals that the CNDs contains rich carbon and oxygen as well as a small amount of nitrogen, and the relative atom ratio of C, O and N is calculated to be 73.31%, 25.12% and 1.57%, respectively. Fig. 2C and D shows high resolution XPS C 1s and O 1s spectra of the CNDs. As shown, C1s spectra (Fig. 2C) exhibit four peaks at 284.3, 285.5, 286.2 and 288.0 eV, corresponding to C−C, C−N, C−O, and C=O bond, respectively. O1s spectra shown in Fig. 2D display two peaks at 531.4 and 532.8 eV, which are attributed to C−OH/C−O−C and C=O bond, respectively. The above results further indicate the CNDs with rich O and N-containing function groups, consistent with FT-IR results. The presence of rich O and N-containing function groups of CNDs is very favorable to improving the interaction between CNDs and CMCZ catalyst, thus forming stable composite catalyst.[44]
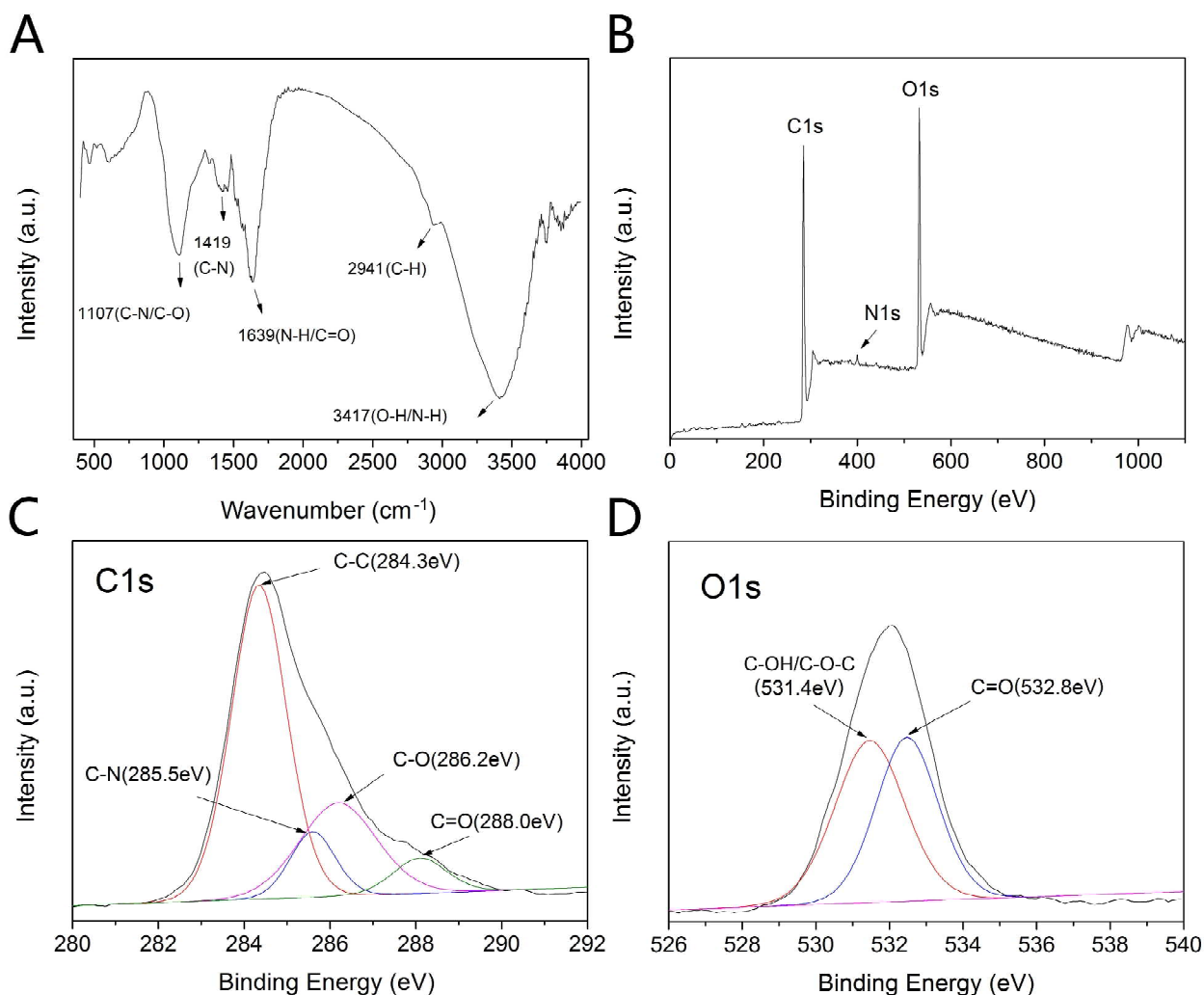
Fig. 2 (A) FT-IR spectra, (B) XPS spectra, (C) High resolution C1s spectra and (D) High resolution O1s spectra.

3.2 Catalytic performance

In order to investigate the influence of the CNDs modification in the catalytic performance of the Cu-Mn-Ce/ZSM (CMCZ) catalyst, the adsorption breakthrough curve of gaseous toluene and the temperature-rising curve of CNDs-CMCZ catalyst were carried out. For comparison, unmodified CMCZ catalyst was also measured under the same experimental conditions. The measured results are shown in Fig. 3. The adsorption breakthrough curves (Fig. 3A) of CMCZ and CNDs-CMCZ revealed that the adsorption breakthrough time of gaseous toluene for CMCZ and CNDs-CMCZ was 25 and 38 min, respectively, and

the loading of CNDs improved apparently the adsorptive capacity of the catalyst within 30-80 min. The increase of adsorption ability is beneficial to improve the degradation efficiency of gaseous toluene on the catalyst surface. The improved adsorptive capacity of CNDs-CMCZ could be due to the enhanced specific surface area which was near 1.5 times higher than that (60.36 $m^2 \cdot g^{-1}$) of CMCZ. The average pore size of the catalyst was decreased from 17.18 nm to 7.71 nm after the modification of CNDs. And the role of surface function groups of the CNDs could also be a reason to the improved adsorptive capacity of CNDs-CMCZ, which deserves a further investigation in future. Under the same experimental conditions, it was found in Fig. 3B that the reaction bed temperature rise of CNDs-CMCZ catalyst was obviously faster than CMCZ catalyst (especially after 50 s under microwave irradiation), and time was shortened almost 45 s while rising temperature from room temperature to 100 °C. The enhanced reaction bed temperature rising speed of the CNDs-CMCZ can be ascribed to the CNDs with rich surface function groups as microwave acceptor to transform the microwave energy into heat (the CNDs acts as "hot spots"),[45] thus improving quickly the reaction bed temperature. Carbon-based materials as microwave acceptor have been widely studied for improving microwave treatment efficiency in many literatures.[46, 47] The concept demonstrated in this work may be beneficial for scale-up application of the CNDs modified catalyst for VOCs treatment.
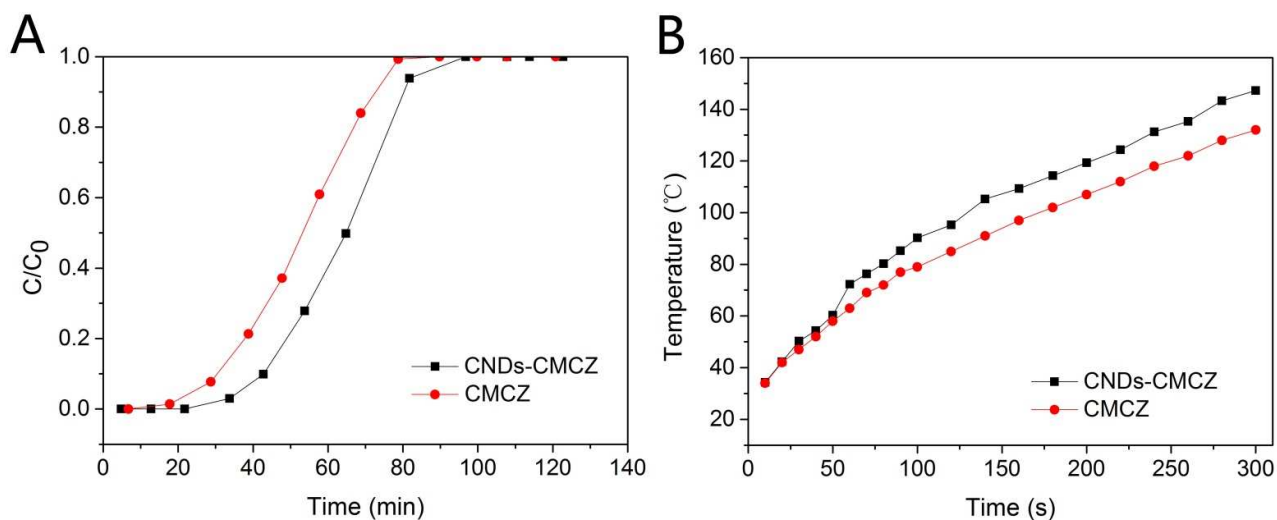

Fig. 3 (A) Adsorption breakthrough curves of gaseous toluene for CMCZ and CNDs-CMCZ catalysts. (B) Temperature-rising curves of CMCZ and CNDs-CMCZ catalysts under microwave irradiation at power of

43.5W.

In order to eliminate adsorption effect, the CMCZ and CNDs-CMCZ catalysts were preliminarily adsorbed toward gaseous toluene for 100 min (based on Fig. 3A) to ensure adsorption equilibrium of the two catalysts, and then the catalytic oxidation reaction was carried out under microwave irradiation. Fig. 4 shows the degradation efficiency of gaseous toluene using CMCZ and CNDs-CMCZ catalysts at different reaction temperatures. As shown, when reaction bed temperature is set at 150 °C, nearly 75% of degradation efficiency of gaseous toluene can be achieved using CNDs-CMCZ catalyst within 80 min, which is almost 1.9 times of that using CMCZ catalyst, indicating a significant influence of CNDs modification on the catalytic performance at relatively low temperature of 150 °C. Compared to MnO_x/γ-alumina and $MnCuO_x/TiO_2$ catalyst with high degradation efficiency for VOCs at near 350 °C, the reaction temperature of toluene oxidation was significantly decreased by CNDs-CMCZ catalyst, which created moderate reaction conditions and less energy consumption. Increasing reaction bed temperature to 200 °C, the degradation efficiency of gaseous toluene is improved to nearly 80% using CNDs-CMCZ catalyst, while 70% of degradation efficiency can be achieved using CMCZ catalyst. When the reaction bed temperature is increased to 250 °C, the degradation efficiency of gaseous toluene can reach ca. 90% for both CMCZ and CNDs-CMCZ catalysts. The above results indicate that high reaction bed temperature is favorable to improving the catalytic performance of the catalyst. However, the effect of CNDs modification on the catalytic performance of catalyst becomes gradually insignificant with increasing reaction bed temperature. Many studies have demonstrated that carbon-based material for microwave treatment of VOCs can not only use as microwave acceptor to absorb microwave energy, but also generate catalytic active sites as catalyst.[48] In this work, at relatively low reaction bed temperature of 150 °C, the significantly improved degradation efficiency of gaseous toluene could be due to a synergistically catalytic role of carbon nanodots and Cu-Mn-Ce/ZSM. Moreover, CNDs should provide a greater contribution on the improved catalytic

performance because the Cu-Mn-Ce/ZSM catalyst has less catalytic active sites at low reaction bed temperature.[42, 49] The role of "hot spots" of CNDs can generate more catalytic active sites even at low reaction bed temperature, which is beneficial for developing low-temperature catalyst for catalytic degradation of VOCs. At higher reaction bed temperature (*e.g.*, 200 °C and 250 °C), the degradation efficiency of gaseous toluene using both CMCZ and CNDs-CMCZ catalysts is obviously enhanced, however, the effect of CNDs on the catalytic performance of catalyst diminishes gradually with increasing reaction bed temperature. This is because higher reaction bed temperature is favorable to generating more catalytic active sites of Cu-Mn-Ce/ZSM catalyst, thus improving the degradation efficiency of gaseous toluene. However, a further carbonization of CNDs at higher temperature may destroy the nanodot structure including surface function groups, leading to decreased influence of carbon nanodots in the catalytic performance. Therefore, the high degradation efficiency of gaseous toluene at higher reaction bed temperature is mainly due to the catalytic role of Cu-Mn-Ce/ZSM, while the degradation efficiency of gaseous toluene using CNDs-CMCZ catalyst at a lower reaction bed temperature (*e.g.*, 150 °C) is ascribed to a synergistic role of carbon nanodots and Cu-Mn-Ce/ZSM.
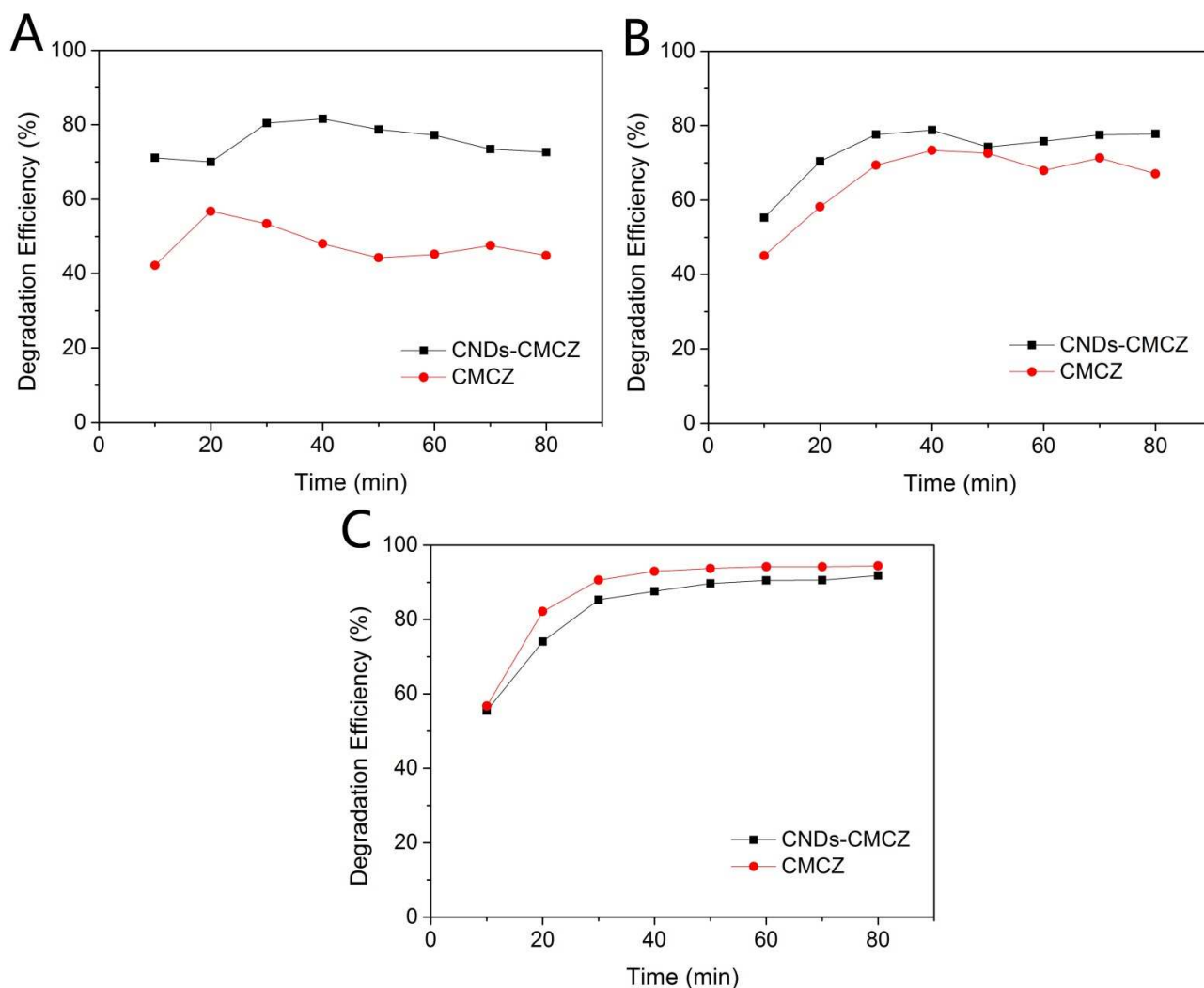
Fig. 4 Catalytic oxidation performance of gaseous toluene using CMCZ and CNDs-CMCZ catalysts at different reaction temperatures. (A) 150°C (B) 200°C (C) 250°C

4. Conclusions

This work has demonstrated a green hydrothermal method to synthesize fluorescent carbon nanodots (CNDs) using dead leaves of plane tree as reaction precursor without any synthetic chemicals. The modification of the CNDs with rich surface O and N-containing function groups obviously enhances the adsorptive capacity and temperature-rising speed of the catalyst, thus improving the catalytic performance at lower reaction bed temperature (*e.g.*, 150 °C), which can be due to a synergistic role of CNDs and Cu-Mn-Ce/ZSM. However, it is believed that the Cu-Mn-Ce/ZSM significantly contributes the improved catalytic performance of the catalysts at higher reaction bed temperature. Our findings demonstrate a

possibility of developing carbon nanodot modified catalyst for low-temperature catalytic oxidation of volatile organic compounds.

Acknowledgments

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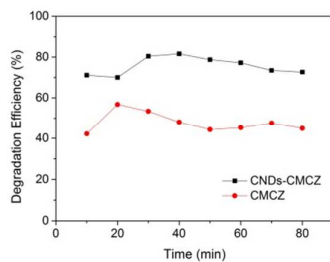
In this figure, toluene waste gas was treated by carbon nanodots (CNDs) modified Cu-Mn-Ce/ZSM catalyst (CNDs-CMCZ) and Cu-Mn-Ce/ZSM catalyst (CMCZ) respectively through a fixed bed under microwave irradiation. It showed that 75% of gaseous toluene was degraded by the CNDs-CMCZ catalyst within 80 min at 150 °C, which was almost 1.9 times of that using unmodified CMCZ catalyst.