RESEARCH ARTICLE

TiO₂ nanosheet supported MnCeOₓ: a remarkable catalyst with enhanced low-temperature catalytic activity in o-DCB oxidation

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Abstract
Morphology engineering was an effective strategy for 1,2-dichlorobenzene (o-DCB) oxidation. Herein, TiO₂ nanosheet supported MnCeOₓ (TiMn₁₅Ce₃₀-NS) showed excellent catalytic activity with T₅₀% = 156 °C and T₉₀% = 238 °C, which was better than the T₅₀% = 213 °C and T₉₀% = 247 °C for TiO₂ nano truncated octahedron supported MnCeOₓ (TiMn₁₅Ce₃₀-NTO). TiMn₁₅Ce₃₀-NS also exhibited enhanced water resistance (T₅₀% = 179 °C, T₉₀% = 240 °C), and good stability with the o-DCB conversion retained at 98.9% for 12 h at 350 °C. The excellent catalytic activity of TiMn₁₅Ce₃₀-NS could be mainly ascribed to the preferentially exposed {001} crystal plane and Ce addition which favored the higher concentration of Mn⁴⁺ and surface active oxygen, along with stronger interaction between MnOₓ and CeOₓ. The present results deepen the understanding of the morphology-dependent effect on o-DCB oxidation.

Keywords TiO₂ nanosheet · MnCeOₓ/TiO₂ · Polychlorinated aromatic hydrocarbons · Catalytic oxidation · o-Dichlorobenzene · Morphology engineering

Introduction
The effective removal of polychlorinated aromatic hydrocarbons (PCAHs) originated from the waste incinerating process has received a widespread concern for the pollutants could result in serious damage to the health of humanity and the eco-environment (He et al. 2019a). Catalytic oxidation has been deemed as a promising approach for PCAH abatement for its low reaction temperature, satisfied degradation performance, and harmless products (Zhang et al. 2018), especially comparing with the generally used strategies such as heat treatment (Lindberg et al. 2015) and physical adsorption (Li et al. 2016). The key issue for decomposing PCAHs is to develop catalysts with high efficiency.

Transition metal oxides such as CeOₓ (Long et al. 2019), FeOₓ (Ma et al. 2014), CrOₓ (Deng et al. 2021), CuOₓ (He et al. 2019b), and MnOₓ (Qiu et al. 2021) have drawn extraordinary interest for the low cost and their strong resistance to chlorine poisoning compared with noble metals which are costly and prone to poison by chlorine species during the catalysis process (van den Brink et al. 2000). In particular, MnO₂ exhibited good reducibility and catalytic activity in PCAHs oxidation among various transition metal oxides (Weng et al. 2019). In addition, the catalytic activity of MnO₂ could be further improved through doping CeO₂ with high oxygen storage capacity (Li et al. 2019a, 2018). MnCeOₓ-based catalysts have been prepared for PCAHs oxidation (Chen et al. 2019), while the current catalysts showed two main drawbacks: (i) high oxidation temperature, for example, MnOₓ/CeO₂ bimetal oxides MnCe(0.43) showed an unsatisfactory catalytic performance for chlorobenzene combustion with the temperature with 90% conversion (T₉₀%) of 279 °C (Wu et al. 2017); (ii) poor water resistance, e.g., Sun et al. (Sun et al. 2016) reported that the MnₓCe₀.₂O₂ showed a severe deactivation in the presence of water due to its competitive adsorption when the temperature was higher than 250 °C. Thus, the further modification of MnCeOₓ-based catalysts to improve the low-temperature catalytic performance along with water resistance for PCAHs oxidation is highly required.
TiO₂ has been used as support in catalytic oxidation (Liu et al. 2001). Recently, researchers have found that catalytic performance of TiO₂ supported catalysts could be modulated through morphology engineering (Wen et al. 2021), which could affect the interface adsorption and reaction centers (Khan et al. 2020). TiO₂ with certain morphology also affected the Lewis acid strength of the catalyst through the geometric arrangement of the surface O²⁻ ligands (Martra 2000). Therefore, morphology engineering of TiO₂ could be used as a strategy for promoting the interaction between the active components and the carrier (Wen et al. 2021), improving the catalytic activity of the catalyst. Our previous study showed that TiFe₅Ca₇₀-S designed by morphology-engineering demonstrated better catalytic activity for o-DCB oxidation with the T₉₀% of 322 °C (Wen et al. 2021), while the low temperature catalytic activity required further improvement. Researchers have also shown that the behavior of H₂O on TiO₂ could be adjusted through facet design (Vittadini et al. 1998), and whether the water resistance in PACHs oxidation could be enhanced through morphology design is another interesting project. Moreover, the detailed oxidation mechanism of o-DCB over the catalysts with certain facet still needs investigation.

Motivated by the above discussion, we attempted to synthesize the catalyst with improved low-temperature catalytic activity and water resistance through morphology-engineering. Herein, TiO₂ catalysts with different morphologies, namely TiO₂ nanosheet (TiO₂-NS) and TiO₂ nano truncated octahedron (TiO₂-NTO), were prepared via hydrothermal treatment. Subsequently, the supported MnCeOₓ/TiO₂ catalysts (TiMn₁₅Ce₃₀-NS and TiMn₁₅Ce₃₀-NTO) were used for the catalytic oxidation of o-DCB (a PCAHs model compound). The relationship between catalytic activity and the morphology of TiMn₁₅Ce₃₀ was investigated. In addition, the reaction intermediates during o-DCB oxidation on MnCeOₓ/TiO₂-NS were explored by in situ diffuse reflectance infrared Fourier transform spectroscopy (in situ DRIFT), and the reaction mechanism was proposed.

**Experimental**

**Catalyst preparation**

TiO₂-NS and TiO₂-NTO were hydrothermally synthesized in this paper. The MnOₓ/TiO₂ and MnCeOₓ/TiO₂ were subsequently prepared by the impregnation method. The experimental details were shown in Supporting Information.

**Catalyst characterization**

Catalyst characterization procedures of TiO₂-NS, TiO₂-NTO, MnOₓ/TiO₂, and MnCeOₓ/TiO₂ such as X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electronic microscopy (TEM), and high-resolution transmission electron microscope (HRTEM), H₂ temperature-programmed reduction (H₂-TPR), X-ray photoelectron spectroscopy (XPS), and in situ DRIFT are described in the Supporting Information.

**Catalyst evaluation**

In this work, the catalytic oxidation of o-DCB was evaluated in a continuous-flow fixed-bed microreactor. During the catalytic evaluation process, the mixed gas (10% O₂, 90% N₂) was divided into two paths, one path flowed through the o-DCB saturated vapor to carry o-DCB, and the other path gas was regarded as balance gas. A third water path (0.5 vol.% water vapor) would be added when the experiment was carried out in the presence of water. The two paths of gas were then fully mixed again. Subsequently, the mixed reaction gas consisting of 50 ppm o-DCB flowed through the fixed catalytic bed reactor with a total flow rate of 60 mL/min. After the catalytic reaction in the reactor, o-DCB in effluent gas was detected using GC1100 gas chromatography with FID detector. The catalytic properties were expressed with the conversion of o-DCB, which was calculated by the following equation,

\[
\chi(\%) = \frac{C_1 - C_2}{C_1} \times 100\%
\]

where C₁ is the initial concentration of o-DCB and C₂ is the final concentration after the catalytic reaction.

**Results and discussion**

**Catalyst characterization**

Figure 1 presents SEM images of TiO₂-NS and TiO₂-NTO and HRTEM images of TiMn₁₅Ce₃₀-NS and TiMn₁₅Ce₃₀-NTO. As shown in Fig. 1a, TiO₂-NS presented a nanosheet-like morphology with 70–160 nm in length, and TiO₂-NTO presented a truncated bipyramid with the edge length of the upper and lower planes of the bipyramid about 30–100 nm (Fig. 1b). HRTEM image of TiMn₁₅Ce₃₀-NS in Fig. 1c showed the lattice spacing of 0.24 and 0.35 nm which could be assigned to the interplanar distances of the {001} plane and {101} plane of anatase phase TiO₂ (Wang et al. 2020a).

Combined the SEM and HRTEM analysis, we presented schematic diagrams of TiMn₁₅Ce₃₀-NS in Fig. 1e, and the flat top and bottom surfaces should be the {001} planes based on the symmetries of anatase TiO₂ (Li et al. 2019b), indicating the preferential exposed {001} plane of TiMn₁₅Ce₃₀-NS catalyst. Similarly, the lattice fringes of
0.36 nm corresponded to the \{101\} plane for the TiO\textsubscript{2} in TiMn\textsubscript{15}Ce\textsubscript{30}-NTO (Fig. 1d) (Leng et al. 2015) and we concluded that TiMn\textsubscript{15}Ce\textsubscript{30}-NTO preferentially exposed \{101\} plane which could be presented as the schematic diagrams in Fig. 1f.

Besides, the nanosheet-like and truncated bipyramid morphology were mainly retained in TiMn\textsubscript{15}Ce\textsubscript{30}-NS (Fig. S1a) and TiMn\textsubscript{15}Ce\textsubscript{30}-NTO (Fig. S1b) and uniformly distributed particles were also observed on the surface after the addition of Mn and Ce. Energy spectrum scanning of TiMn\textsubscript{15}Ce\textsubscript{30}-NS revealed that four elements including Mn, Ce, O and Ti were detected on the surface of the catalyst (Fig. 2), demonstrating that Mn and Ce were successfully supported on TiO\textsubscript{2} nanosheet.

The XRD patterns of anatase TiO\textsubscript{2}-NS, TiO\textsubscript{2}-NTO, TiMn\textsubscript{15}Ce\textsubscript{30}-NS, and TiMn\textsubscript{15}Ce\textsubscript{30}-NTO were presented.
in Fig. 3, and the results showed that the peaks of TiO2-NTO and TiO2-NS were consistent with the anatase phase TiO2 (JCPDS 21–1272) (Gui et al. 2009). After loading Mn, the corresponding peaks of TiMn15-NS did not change significantly (Fig. S2). With the loading of Ce in TiMn15-NS, the peak at 28.9° attributing to MnO2 (110) (JCPDS 24–0735) crystal plane was observed (Cao et al. 2017). The average crystal sizes of TiO2-NS, TiO2-NTO, TiMn15Ce30-NS, and TiMn15Ce30-NTO were calculated by Scherrer equation based on the (101) diffraction peak of TiO2 (Table S1). Noticeably, the grain size was 43.8 nm in TiO2-NS, and the value reduced to 34.2 nm in TiMn15Ce30-NS, demonstrating the crystal size of TiO2 was refined by introducing Mn and Ce, while the counterpart data in TiMn15Ce30-NTO increased to 40.0 nm from 37.9 nm in TiO2-NTO, which could be explained by that the TiO2 particles in TiO2-NTO with mainly {101} plane were more likely to aggregate with Mn/Ce loading during calcination according to previous reports (Deng et al. 2016). It is well-known that smaller grain size endows more abundant surface area or interface area, which might provide more defect sites for catalytic reactions, promoting catalytic activity (Zhao et al. 2020b).

Deng et al. (Deng et al. 2016) have proved that the preferential exposure of the (001) crystal plane of TiO2 crystal was related to the broader peak of the (004) diffusion and the narrower peak of (200). As can be seen in Table S1, the full width at half maximum (FWHM) of TiMn15Ce30-NS (004) (0.312°) peak was larger than that of TiMn15Ce30-NTO (0.192°), while its FWHM of (200°) peak (0.223°) was smaller than the corresponding data of 0.227° for TiMn15Ce30-NTO. This phenomenon further proved that TiMn15Ce30-NS preferentially exposed {001} crystal plane as obtained in Fig. 1.

Figure 4 depicts the N2 adsorption/desorption isothermal of pure TiO2, TiMn15-NS, and TiMn15Ce30-NS. TiO2-NS showed I-type isotherm (IUPAC) (Rahman et al. 2019), and its curve increased slightly in the relative pressure ranging from 0.0 to 0.2 ascribed to micropore filling (Abebe et al. 2018), implying that TiO2-NS mainly possessed microporous. The TiMn15-NS was presented as a type IV isotherm, and it displayed an H3-type hysteresis loop at relative pressure from 0.75 to 1.0; besides, the rapid rise during the relative pressure from 0.85 to 1.0 might be attributed to the condensation of adsorbate gas (Abebe et al. 2018). After the introduction of Ce, the isotherm of TiMn15Ce30-NS retained type IV, and the H3-type hysteresis loop appeared at P/P0 of 0.7 ~ 1.0.

Table 1 summarizes the specific surface area and average pore diameter of catalysts. The average pore size of TiO2-NS was 1.41 nm, and the value was 7.83 nm in TiMn15-NS, indicating that TiMn15-NS mainly possessed mesoporous. Moreover, the specific surface area of TiMn15-NS was 32.0
Comparing to the 19.8 m²/g in TiO₂-NS attributed to the loading of Mn. The specific surface area of TiMn₁₅Ce₃₀-NS did not change significantly after further loading Ce, while TiMn₁₅Ce₃₀-NS presented a hierarchical porous structure with a relatively wide pore distribution at 8.78, 17.63, and 36.51 nm ranging from 2 to 86 nm (Fig. 3), indicating the coexistence of mesoporous and macroporous. Studies have reported that the mesoporous could provide relatively higher internal specific surface area (Liu and He, 2010), and the macroporous possessed relatively small diffusion resistance, which is conducive to the mass transfer process (Arandiyán et al. 2018). Thereby, we could reasonably deduce that the wide range of the porous structure of TiMn₁₅Ce₃₀-NS may be favorable for o-DCB diffusion and adsorption on TiMn₁₅Ce-NS, promoting the catalytic oxidation activity.

The reduction performances of TiO₂-NS, TiMn₁₅-NS, and TiMn₁₅Ce₃₀-NS were studied through H₂-TPR with the results reflected in Fig. 5. The reduction temperature of pristine TiO₂-NS was 658 °C. After loading Mn on the TiO₂-NS, the reduction temperature of TiO₂ in TiMn₁₅-NS decreased to 636 °C. In addition, two new reduction peaks centered at 265 °C assigned to the reduction of MnO₂ to Mn₂O₃ and 335 °C attributed to the transformation of Mn₂O₃ to Mn₃O₄ were observed (Chen et al. 2018). The peak at 447 °C can be attributed to the reduction of MnO₂ to MnO (Zhao et al. 2019a). For TiMn₁₅Ce₃₀-NS, the temperature of MnO₂ to Mn₂O₃ and Mn₂O₃ to Mn₃O₄ decreased to 236 °C and 297 °C, respectively. The peak attributed to MnO₂ reduction to MnO was also reduced to 396 °C on the TiMn₁₅Ce₃₀-NS curve (Wu et al. 2019). These results revealed that the addition of Ce significantly affected the reduction temperatures of MnO₂, proving that the loading of Ce contributed to the electron transfer between MnO₂ and CeO₂, and promoted the migration of surface oxygen or lattice oxygen (Zhao et al. 2019b), consequently improving the reduction performance of MnO₂ (Wang et al. 2013). Note that the peak at 466 °C corresponded to the reduction of CeO₂ on the catalyst surface to Ce₂O₃ (Zhao et al. 2019a).

XPS was used to characterize the surface properties of the TiMn₁₅-NS and TiMn₁₅Ce₃₀-NS. Fig. 6a shows the Mn 2p spectrum of the catalysts, the peaks observed at 641.8 eV and 653.3 eV corresponded to Mn³⁺, and the peaks at 643.1 eV and 654.7 eV were attributed to Mn⁴⁺ (Ferrel-Álvarez et al. 2018). It is widely established that the higher ratio of Mn⁴⁺ can introduce more available oxygen species (Wang et al. 2020b) and facilitate the redox cycling during reaction processes, which could promote catalytic activity (Geng et al. 2020). The relative surface Mn⁴⁺ ratio calculated by Mn⁴⁺/(Mn³⁺ + Mn⁴⁺) was displayed in Table 2, the surface Mn⁴⁺ content on TiMn₁₅-NS was 65.8%, and the value increased to 76.7% with introducing Ce. The phenomenon further elucidated that the addition of Ce was favorable for the electron transformation between Ce and Mn through the

| Samples             | S_{BET} [a] (m²/g) | V_p [a] (cm³/g) | D_p [a] (nm) |
|---------------------|-------------------|----------------|-------------|
| TiO₂-NS             | 19.8              | 0.05           | 1.41        |
| TiMn₁₅-NS           | 32.0              | 0.06           | 7.83        |
| TiMn₁₅Ce₃₀-NS       | 32.0              | 0.07           | 6.83        |

[a]Structure parameters of the catalysts calculated via N₂ isotherm; S_{BET}, BET surface area; V_p, total pore volume; D_p, average pore diameter.
equilibrium of 
\[\varepsilon Mn^3 + e + \varepsilon Ce^4 + e \leftrightarrow \varepsilon Mn^4 + e + \varepsilon Ce^3 + e\] (Wan et al. 2022).

The O1s peaks can be deconvoluted into two parts (Fig. 6b): the binding energies at 528.1–531.2 eV corresponding to lattice oxygen \(O^{2-}\) (denoted as \(O_\beta\)) and the one at 528.1–534.8 eV ascribing to the surface oxygen species (denoted as \(O_\alpha\)), such as \(O^-\) from the defect-oxide or \(OH^-\) ascribed to the hydroxyl-like group (Chen et al. 2017). And the relative concentration of surface oxygen species was calculated by \(O_\alpha/(O_\alpha + O_\beta)\) as listed in Table 2. The area ratio of \(O_\alpha/(O_\alpha + O_\beta)\) in TiMn15Ce30-NS (46.4%) was higher than that in TiMn15-NS (34.1%), indicating that the addition of Ce increased the concentration of reactive oxygen species.

**Catalytic performance of the prepared catalysts in \(\sigma\)-DCB oxidation**

The conversion of \(\sigma\)-DCB as a function of temperature over TiO\(_2\)-NTO, TiO\(_2\)-NS, TiMn15-NS, and TiMn15-NTO were shown in Fig. 7. It can be seen that the activity of TiO\(_2\)-NS was higher than that of TiO\(_2\)-NTO in the entire temperature range. For example, the \(\sigma\)-DCB conversion rate of TiO\(_2\)-NS was 38.2% at 350 °C, which was much higher than 15.6% of TiO\(_2\)-NTO, suggesting that the crystal plane of TiO\(_2\) significantly affected the \(\sigma\)-DCB oxidation, and the fact that TiO\(_2\)-NS with preferentially exposed \{001\} facet exhibited good catalytic activity could be explained by the abundant amount of unsaturated coordinated Ti atoms on the \{001\} crystal plane favored high chemical activity, favoring the \(\sigma\)-DCB adsorption and oxidation (Liu et al. 2016). The above result is in agreement with our previous study (Wen et al. 2021). TiO\(_2\)-NS doped with different amount of Mn or Ce were investigated. As illustrated in Fig. S3, the TiO\(_2\)-NS with 15 mol% of Mn/(Ti + Mn) exhibited notably higher catalytic performance for \(\sigma\)-DCB oxidation. Therefore, TiMn15-NS and TiMn15-NTO were synthesized and

![XPS profiles of TiMn15-NS and TiMn15Ce30-NS](image)

**Fig. 6** XPS profiles of TiMn15-NS and TiMn15Ce30-NS **a** Mn 2p, **b** O1s

| Samples          | Surface atomic ratio \(^a\) (%) | \(\varepsilon Mn^4+/\varepsilon (Mn^3+ + Mn^4+)\) | \(O_\alpha/(O_\alpha + O_\beta)\) |
|------------------|--------------------------------|-----------------------------------------------|---------------------------------|
| TiMn15-NS        | 65.8                           | 65.8                                          | 34.1                            |
| TiMn15Ce30-NS    | 76.7                           | 76.7                                          | 46.4                            |

\(^a\)Surface atomic ratios were calculated based on the peak areas of binding energy

![Light-off curves for the catalytic oxidation of \(\sigma\)-DCB over TiO\(_2\)-NS and TiO\(_2\)-NTO and TiMn15-NS and TiMn15-NTO](image)

**Fig. 7** Light-off curves for the catalytic oxidation of \(\sigma\)-DCB over TiO\(_2\)-NS and TiO\(_2\)-NTO and TiMn15-NS and TiMn15-NTO. (50 ppm DCB, 10% \(O_2\), WHSV = 36,000 mL/(g·h))
In addition, as obtained in Fig. 7, TiMn15-NS still presented superior activity with the T_{50\%} of 234 °C than that of 266 °C in TiMn15-NTO.

Moreover, the oxidation activity of TiMn15-NS was further improved when doping with 30 mol% of Ce in TiMn15Ce30-NS as suggested in Fig. S3. Similarly, TiMn15Ce30-NS also exhibited better oxidation activity than TiMn15Ce30-NTO (Fig. 8). For instance, the T_{50\%} of TiMn15Ce30-NS was 156 °C, and the value was 213 °C for TiMn15Ce30-NTO. These results further confirmed the influence of the crystal plane of TiO_2 on -DCB decomposition, which be closely associated with the preferentially exposed {001} crystal plane of TiMn15Ce30-NS (Wen et al. 2021). In addition, based on the results in Figs. 7 and 8, it showed that introduction of CeO_2 on both TiMn15-NS and TiMn15-NTO significantly increased the activity for -DCB oxidation. Especially for the TiMn15Ce30-NS, it exhibited excellent low temperature catalytic activity than TiMn15Ce30-NTO. Given the results mentioned above, the excellent catalytic activity of TiMn15Ce30-NS for -DCB decomposition could be explained as follows. Firstly, TiMn15Ce30-NS with preferential exposed {001} crystal plane has more oxygen vacancies (Li et al. 2019b), which could provide more adsorption sites for gas molecules (Liu et al. 2009). Moreover, the addition of Ce improved the low-temperature reducibility of MnO_x through contributing the interaction between MnO_2 and CeO_x in TiMn15Ce30-NS (Wan et al. 2022). Besides, the addition of Ce contributed a higher content of Mn^{4+} and O_α in TiMn15Ce30-NS than those of TiMn15-NS according to the XPS results, which facilitated redox cycles between Mn^{3+} and Ce^{4+}, enhancing the migration of oxygen species (Wan et al. 2022). Noteworthy, the current TiMn15Ce30-NS exhibited a significantly superior catalytic performance with the T_{50\%} of 238 °C compared with the TiFe5Ca70-S (322 °C) under the same space velocity condition (Wen et al. 2021), suggesting that the catalytic activity of MnCeO_x/TiO_2 for decomposing -DCB could be further improved.

Water is an inevitable component in the actual flue gas, and the presence of water has an important effect on the catalytic oxidation PCAHs (Ma et al. 2016). As shown in Fig. 8, in the presence of water (0.5 vol.% H_2O), the activity of TiMn15Ce30-NS in the low-temperature region (< 200 °C) was inhibited to some extent, which was most likely ascribed to the competition adsorption between the H_2O and -DCB on active sites of the catalyst surface (Hetrick et al. 2011). When the temperature was higher than 200 °C, the -DCB conversion increased with the total conversion of -DCB was still obtained at 300 °C. Moreover, the overall activity of TiMn15Ce30-NS with T_{50\%} of 179 °C and T_{90\%} of 240 °C was still clearly better than that of TiMn15Ce30-NTO with T_{50\%} of 205 °C and T_{90\%} of 246 °C under humid conditions. The above results suggested that the crystal plane also affected the catalytic performance of -DCB oxidation in humid condition (Wen et al. 2021), which might be explained by that the nanosheet morphology TiO_2 [001] crystal surface allowed more hydroxyl groups to combine with the ortho Ti sites to generate more acidic sites (Wen et al. 2018) which could facilitate the adsorption of -DCB (Li et al. 2021; Sun et al. 2016) and favor H_2O dissociation more easily compared with TiO_2 [101] crystal surface (Vittadini et al. 1998), thus reducing the negative effect of competitive adsorption of H_2O with -DCB.

The lifetime of TiMn15-NS and TiMn15Ce30-NS for -DCB oxidation was evaluated at 350 °C (Fig. 9). TiMn15Ce30-NS exhibited excellent stability with -DCB conversion retained at 98.9% for 12 h. However, for TiMn15-NS, the corresponding conversion decreased to 83.5%. The higher stability of TiMn15Ce30-NS could be also explained by its nanosheet structure with preferentially exposed {001} facet that allowed more hydroxyl groups to combine with the ortho Ti sites, thus generating more Bronsted acidic sites (Wen et al. 2018), and favor H_2O dissociation more easily (Vittadini et al. 1998) to provide H^+, thus favoring the removal of Cl^- species through forming HCl, maintaining a relatively stable activity. In brief, TiO_2 nanosheet supported MnCeO_x/TiO_2 (TiMn15Ce30-NS) showed excellent low-temperature catalytic activity, enhanced water resistance, and good stability for -DCB oxidation, which was significantly better than most of the previous reported Mn-based catalysts as shown in Table 3.
In situ FT-IR analysis of TiMn15Ce30-NS

Transient reaction processes by in situ DRIFT spectra were performed to identify various reactive species and deduce a possible mechanism of the reaction. The DRIFT spectra collected at different time intervals during the adsorption and oxidation of o-DCB over TiMn15Ce30-NS at 300 °C were shown in Fig. 10a. The weak peak of 1283 cm⁻¹ (C-O stretching vibration) was assigned to the phenols (Lichtenberger 2004), and the band at 1410 cm⁻¹ was associated with the formation of the o-benzoquinone (Lichtenberger 2004). It is widely accepted that the initial stage of o-DCB oxidation mainly includes the dissociative adsorption of o-DCB and nucleophilic substitution reaction. The lone pair electrons of the Cl atom are captured by the Lewis acid sites, causing a nucleophilic attack on the position of chlorine and breaking the C–Cl bonds, and then o-DCB adsorbed on the active sites of transition metal oxides, generating phenolics via the reaction with surface oxygen (Lichtenberger 2004; Ma et al. 2013). Moreover, the o-DCB molecules can react at the Brønsted acid sites and produce HCl during the oxidation process according to Taralunga (Taralunga et al. 2006). Consequently, the characteristic peak of 1283 cm⁻¹ corresponded to the symmetric -COO- stretching vibration of the surface formates species (Krishnamoorthy et al. 2000). The peaks at 1360 cm⁻¹ and 1540 cm⁻¹ were ascribed to the formation of carboxylates (acetates type) (Krishnamoorthy et al. 2000; Ma et al. 2016). Hence, it can be deduced that the o-benzoquinone was oxidized to formates and acetate over the TiMn15Ce30-NS. The weak peaks at 2320 cm⁻¹ and 2355 cm⁻¹ were assigned to the CO₂ (Silva et al. 2018), indicating that the intermediate formates and acetic species were further converted to CO₂ by deep oxidation. Besides, in addition to the intermediates mentioned above, the o-DCB catalyzed oxidation process is usually accompanied by the formation of H₂O, which can be explained from our previous studies (Ma et al. 2019).

Figure 10b shows the in situ DRIFT spectra over TiMn15Ce30-NS collected at 100, 200, and 300 °C after 20 min reaction. As can be seen, the intensity of formates (1374 cm⁻¹), acetates (1360 cm⁻¹), and surface carbonates (1540 cm⁻¹) were significantly enhanced when increasing the reaction temperature to 200 °C from 100 °C, demonstrating that the dechlorination, ring-opening, and catalytic oxidations of chlorobenzene were effectively improved.

Table 3 The states of the arts of Mn-based catalysts for PCAHs oxidation

| Catalysts                  | Pollutant   | Reaction conditions               | T₅₀/T₉₀ (°C) | Ref          |
|----------------------------|-------------|----------------------------------|-------------|--------------|
| TiMn15Ce30-NS              | o-DCB       | 50 ppm, 10% O₂/N₂, 36,000 mL·g⁻¹·h⁻¹ | 156/238     | This work    |
| MnOₓ-D                     | o-DCB       | 1000 ppm, 20% O₂/N₂, 15,000 mL·g⁻¹·h⁻¹ | 238/321     | (Ling et al. 2020) |
| CeMnOₓ-rods                | o-DCB       | 1000 ppm, 20% O₂/N₂, 15,000 mL·g⁻¹·h⁻¹ | 293/346     | (Zhao et al. 2019a) |
| CeMn30                     | o-DCB       | 1000 ppm, 20% O₂/N₂, 15,000 mL·g⁻¹·h⁻¹ | 291/347     | (Yang et al. 2019) |
| 5.0%/Ce/OMS                | o-DCB       | 1000 ppm, 60,000 mL·g⁻¹·h⁻¹, 5% vol of H₂O | >300/>335   | (Chen et al. 2019) |
| Mn/Co (0.50)               | Chlorobenzene | 1000 ppm, 20% O₂/N₂, 15,000 mL·g⁻¹·h⁻¹ | 165/231     | (Hu et al. 2018) |
| 15CM/TiS-1.5               | o-DCB       | 500 ppm, 20% O₂/N₂, 15,000 mL·g⁻¹·h⁻¹ | >300/>360   | (Zhao et al. 2018) |
| MCZ-0.67                   | Chlorobenzene | 1000 ppm, 21% O₂/N₂, 20,000 h⁻¹ | >175/226    | (Zhu et al. 2019) |
| Mn-Ce-Zr ternary mixed oxides | o-DCB       | 1000 ppm, 21% O₂/N₂, 30,000 h⁻¹ | 320/>390    | (Long et al. 2019) |
| Mn-Ce-Fe                   | o-DCB       | 600 ppm, 12,000 mL·g⁻¹·h⁻¹            | 253/380     | (Tang et al. 2016) |
| 30Cu/MnOₓ                  | Chlorobenzene | 1000 ppm, 20% O₂/N₂, 15,000 h⁻¹    | >150/290    | (Chen et al. 2020) |
| MnOₓ/CoOₓ-4 h              | Chlorobenzene | 1000 ppm, 20% O₂/N₂, 60,000 mL·g⁻¹·h⁻¹ | >275/>330   | (Hu et al. 2021) |
| CoMn600@0.5Ti              | Chlorobenzene | 1000 ppm, 20% O₂/N₂, 15,000 mL·g⁻¹·h⁻¹ | 341/392     | (Zhao et al. 2020a) |
oxidation reactions took place over TiMn15Ce30-NS at 200 °C during o-DCB decomposition. When increasing the temperature to 300 °C, the intensity of formates, acetates, and surface carbonates all weakened obviously, meanwhile the peaks of CO₂ at 2320 cm⁻¹ and 2355 cm⁻¹ slightly increased. Therefore, it can be deduced that increasing temperature in a certain range (particularly from 200 to 300 °C) could promote the deep oxidation of o-DCB to CO₂ over TiMn15Ce30-NS.

Based on the mentioned above, the catalytic oxidation mechanism of o-DCB over TiMn15Ce30-NS can be elucidated in Fig. 11. As reported previously (Mahmood et al. 2019), TiO₂ {001} crystal planes endow abundant fivefold under-coordinated Ti atoms and twofold coordinated oxygen sites which were proved to be the adsorption active sites; we hence deduce that the o-DCB was prone to adsorb on the {001} facet of TiMn15Ce30-NS. Subsequently, the adsorbed o-DCB transformed into phenolic species and then o-benzoquinone through nucleophilic substitution. Afterward, formates and acetate species were formed via a ring-opening reaction of o-benzoquinone, and these species were finally oxidized to CO₂ and H₂O.

Conclusions

Morphology engineered TiO₂-NS and TiO₂-NTO supported MnCeOₓ in o-DCB oxidation was investigated. TiMn15Ce30-NS exhibited better low temperature catalytic activity with T₅₀% = 156 °C, T₉₀% = 238 °C comparing with T₅₀% = 213 °C and T₉₀% = 247 °C for TiMn15Ce30-NTO. TiMn15Ce30-NS also showed superior water resistance (T₅₀% = 179 °C, T₉₀% = 240 °C), as well as excellent stability with the o-DCB oxidation conversion above 98% for 12 h at 350 °C, which verified the crucial influence of preferentially exposed {001} plane on o-DCB oxidation. The good catalytic performance of TiMn15Ce30-NS could be explained by the morphology engineering and Ce addition that improved its reducibility, surface oxygen species concentration, and higher ratio of Mn⁴⁺. This work provided an important clue for catalyst design through morphology engineering.
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Data availability All relevant data generated or analyzed during this study were included in this published article.

Declarations

Ethics approval and consent to participate This manuscript does not contain any studies with human participants or animals performed by any of the authors.

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