Two-dimentional manganese oxide on ceria for the catalytic partial oxidation of hydrocarbons

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Abstract

Although the rational synthesis of catalysts with strong oxide-support interactions to modulate the geometric and electronic structures and achieve unusual catalytic performance is challenging in heterogeneous catalysis, it is in significant demand for the efficient and sustainable transformation of chemicals. Here, we report the synthesis and performance of a ceria-supported two-dimensional manganese oxide catalyst with strong metal oxide-support interactions, which help to produce well-dispersed and amorphous MnOₓ layers on the CeO₂ matrix (MnOₓ/CeO₂). This catalyst readily reacts with molecular oxygen to give a high capacity of active oxygen species, owing to the interfacial effect. The C-H bonds are adsorbed and activated by these active interfacial oxygen species, leading to high activities and selectivities in the industrially important C-H bond activation reactions, such as the oxidation of hydrocarbons to alcohols and ketones with molecular oxygen under solvent- and initiator-free
conditions at mild temperature. The performance of the MnOₓ/CeO₂ catalyst is greater than that of noble metal and highly efficient Mn-Ce solid-solution catalysts. More importantly, the catalyst is stable and exhibits constant reactivity in continuous recycling tests. These results are important for the design of highly efficient catalysts for the selective oxidation of hydrocarbons.

Keywords: Strong oxide-support interactions, C-H oxidation, MnOₓ/CeO₂ catalyst, heterogeneous catalysis

INTRODUCTION

The oxidation of \(sp^3\)-hybridized C-H bonds has emerged as a facile and industrially important process for the sustainable production of alcohols, ketones and epoxides from petroleum hydrocarbons\(^{[1-4]}\). Generally, the inorganic salts of ClO\(^4\)⁻ and NO\(^3\)⁻ are used as oxidants, which are costly and environmentally unfriendly\(^{[5]}\). Although molecular oxygen is regarded as a favorable oxidant, harsh reaction conditions are necessary for the activation of strong C-H bonds, which generally leads to significant energy consumption and uncontrollable selectivities\(^{[6-9]}\). In addition, over-oxidation occurs in many cases to produce carbon dioxide and other byproducts, particularly during vapor-phase oxidation\(^{[3,10]}\). As an attractive process in industry, the liquid-phase oxidation of C-H bonds has attracted tremendous attention, but the conversion of hydrocarbon substrates is always unsatisfactory. Subsequently, noble metal catalysts, peroxide initiators, organic solvents, supercritical CO\(_2\) and ionic liquid additives are used for enhancing the substrate conversion\(^{[11-16]}\), but new problems arise, such as increased costs and extra product purification. Therefore, the efficient catalytic oxidation of C-H bonds with molecular oxygen over non-noble metal catalysts, as well as avoiding the use of solvents and initiator additives, remains challenging.

Mn-Ce oxides have been extensively investigated as efficient catalysts for the total oxidation of NO\(^{[17]}\), CO\(^{[18-23]}\) and organic molecules for pollutant removal\(^{[24-28]}\), because of their high activity toward the activation of molecular oxygen. The features of Mn-Ce oxides in molecular oxygen activation have also motivated research into the selective oxidation of C-H bond and excellent success has been achieved. For example, Mn-Ce oxides were synthesized with surfactants or ionic liquids to maximize the solid-solution phase, which readily exhibited superior activity and selectivity for the selective oxidation of hydrocarbons\(^{[18]}\). However, organic solvents are still necessary in most of these cases\(^{[18]}\). Furthermore, the expensive surfactants and ionic liquids still limit their practical applications. Developing strategies for the synthesis of efficient Mn-Ce catalysts therefore remains a vital area of research in this field.

Here, we report a ceria-supported two-dimensional manganese oxide catalyst that is highly efficient for the selective oxidation of hydrocarbons without the use of solvents and initiator additives. The key to this success is anchoring the two-dimensional and amorphous manganese oxide layers on the cerium matrix (MnOₓ/CeO₂) via strong oxide-support interactions (SOSIs). Owing to these features, the catalyst readily reacts with molecular oxygen to give a high capacity of active oxygen species at 46.1%. In the solvent- and initiator-free oxidation of C-H bonds on a series of hydrocarbons with molecular oxygen at low temperatures, the MnOₓ/CeO₂ catalyst exhibits high activities and selectivities, as well as good stabilities in the recycling tests (Scheme 1). For example, in the aerobic oxidation of ethylbenzene, it gives a conversion of 63.5% and a selectivity of 95.7% to the corresponding alcohol/ketone products, thereby outperforming highly efficient heterogeneous catalysts under solvent- and initiator-free systems reported in the literature.

EXPERIMENTAL

Synthesis

**Synthesis of MnOₓ/CeO₂ catalysts**

As a typical synthesis of the MnOₓ/CeO₂(0.05) [where 0.05 is the theoretical Mn/(Mn + Ce) molar ratio]
catalyst, 6 g of cerium nitrate [Ce(NO$_3$)$_3$$ \cdot $6H$_2$O] and 0.26 g of a manganese nitrate aqueous solution (50 wt.%) were dissolved in 5 g of ethanol and 5 g of deionized water in flask A and stirred at room temperature for 20 min. Meanwhile, 2 g of glycerol and 4.8 g of citric acid monohydrate were dissolved in 5 g of ethanol and 5 g of deionized water in flask B and stirred at room temperature for 20 min. After that, the liquor in flask B was added to flask A with continuous stirring at room temperature for 3 h and 90 °C for 3 h in a closed reactor. Finally, the ethanol and water solvent was volatilized to obtain a foamed solid. After drying at 100 °C overnight and calcining at 800 °C for 4 h in air to remove the organic species, the MnO$_x$/CeO$_2$ catalyst was finally obtained. CeO$_2$ and MnO$_x$/CeO$_2$(y) catalysts with Mn/(Mn + Ce) molar ratios of 0.025, 0.1, 0.2 and 0.3 were synthesized using the same procedure by adjusting the amount of the manganese nitrate aqueous solution in the starting solutions. Accordingly, the samples were termed as CeO$_2$, MnO$_x$/CeO$_2$(0.025), MnO$_x$/CeO$_2$(0.1), MnO$_x$/CeO$_2$(0.2) and MnO$_x$/CeO$_2$(0.3), respectively.

**Synthesis of acid-treated MnO$_x$/CeO$_2$(0.05)**

First, the acid-treated MnO$_x$/CeO$_2$(0.05) catalyst was synthesized by washing the as-synthesized MnO$_x$/CeO$_2$(0.05) with diluted hydrochloric acid (20%) at 90 °C for 4 h. The solid was then collected by centrifugation and washed with a large excess of deionized water and dried in air at 100 °C overnight. Finally, the sample was calcined in air at 400 °C for 2 h in a rotating quartz tube to obtain the acid-treated MnO$_x$/CeO$_2$(0.05) catalyst.

**Synthesis of MnO$_x$/CeO$_2$ and MnO$_x$/SiO$_2$**

For comparison, MnO$_x$/CeO$_2$ with an Mn/(Mn + Ce) molar ratio at 0.05 was also prepared by an incipient wetness co-impregnation method. In a typical run, an Mn(NO$_3$)$_2$ aqueous solution (50 wt.%) was used as a precursor and CeO$_2$ was used as a support (CeO$_2$ was prepared by the citric acid-assisted method discussed above). After impregnation, the catalysts were placed in the atmosphere statically overnight and then dried in an oven and calcined at 600 °C for 4 h in air. The resulting catalyst was denoted as MnO$_x$/CeO$_2$. 

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**Scheme 1.** Synthetic and catalytic strategies for ceria-supported two-dimensional manganese oxide catalyst with strong oxide-support interactions.
MnO$_x$/SiO$_2$ was also synthesized by the same procedure for MnO$_x$/CeO$_2$ but using SiO$_2$ as the support.

**Catalysis**

*Catalytic oxidation of hydrocarbons*

The oxidation of hydrocarbons in the liquid phase was performed with a high-pressure autoclave reactor equipped with a magnetic stirrer (900 rpm). In a typical run, the catalyst and hydrocarbon were mixed in the reactor and pure oxygen was used for the reaction. The autoclave was purged with oxygen three times to remove the air in the autoclave before the reaction. Oxygen was then introduced to the desired pressure. Next, the reactor was rapidly heated to the desired temperature (the reaction temperature was measured by a thermocouple in the autoclave and the pressure was measured at the reaction temperature). After the reaction, the reactor was placed in an ice bath to stop the reaction, and bromobenzene or biphenyl was used as the internal standard. In the stability test, the catalyst was removed from the reactor and washed with ethanol after each reaction run, dried overnight at 150 °C and then used in the next experiment to evaluate its recyclability.

The products were analyzed by gas chromatography (GC-14C, Shimadzu, with a flame ionization detector and ethanol or acetonitrile used to dilute the liquor before the analysis) with a flexible quartz capillary column (OV-17). The gas-phase products (e.g., CO or CO$_2$ produced from over-oxidation) were analyzed using a Fu Li-9790 gas chromatograph equipped with a thermal conductivity detector (TCD). The as-synthesized catalyst was used each time to make sure the reactions were conducted under identical conditions. High-pressure oxygen has been extensively used in aerobic oxidations and the reaction systems in this work were out of the explosion limits of the reactants. For example, the explosion limit of ethylbenzene is 1.0%-7.1% in oxygen and the concentration of ethylbenzene in the gaseous phase in this work is out of the explosion limit. Fire and static electricity were therefore avoided for safety reasons.

*Catalytic oxidation of CO*

The oxidation of CO was performed in a continuous-flow fixed-bed quartz vertical reactor (length of 400 mm and internal diameter of 6 mm) in a temperature controllable oven. First, 0.2 g of catalyst (40-60 mesh) diluted with 0.6 g of quartz sands (40-60 mesh) were located in the reactor. The feed gas containing 1% CO and 18% O$_2$ in He was introduced with a total rate of 20 sccm. The concentration of CO in the feed and emission gases was continually monitored by the chromatograph equipped with the TCD detector. In the kinetic study, the partial pressure of CO was controlled by adjusting the flow rate of CO and the total rate was balanced with He.

**Characterization**

*Temperature-programmed desorption*

The temperature-programmed desorption of O$_2$ (O$_2$-TPD) was measured in a BELCAT II catalyst analyzer equipped with a TCD. As a typical run, 30 mg of solid catalyst were pretreated at 600 °C for 1 h in air before the measurement and then cooled to 50 °C. The sample was then heated to 800 °C at a ramp rate of 10 °C/min for detecting the desorbed oxygen species.

*In-situ Fourier transform infrared spectroscopy*

The in-situ Fourier transform infrared (FTIR) spectra were recorded using a Nicolet iS50 FTIR spectrometer equipped with an MCT/A detector, ZnSe windows and a high temperature reaction chamber. As a typical run, 50 mg of MnO$_x$/CeO$_2$(0.05) were localized in the sample chamber and pretreated at 120 °C for 1 h in flowing Ar (30 sccm) and then cooled to room temperature. The steam containing ethylbenzene (partial pressure in the range of 9-16 mbar) was introduced into the system with a flow of Ar carrier gas (30 sccm). After adsorption for 1 h at room temperature, a pure Ar gas was introduced to purge the sample for another
1 h and the FTIR spectrum of ethylbenzene adsorbed on the solid sample was then recorded. After increasing the reaction temperature to 160 °C in flowing Ar and maintaining it for 30 min, the FTIR spectra were recorded to understand the interaction between ethylbenzene and the active oxygen species on the catalyst surface. Whilst maintaining the temperature of the chamber at 160 °C, oxygen was introduced to further promote the interaction, where the FTIR spectra were recorded to detect the formation of carbon-oxygen species.

To investigate the crucial role of the active oxygen species on the catalyst, we eliminated the oxygen by H₂ reduction during the in-situ FTIR study. In a typical run, 50 mg of the MnOₓ/CeO₂(0.05) sample were pretreated at 200 °C with 10% H₂/Ar for 2 h and then cooled to room temperature. The steam containing ethylbenzene was then introduced into the system with a flow of Ar carrier gas (30 sccm). After adsorption for 1 h at room temperature, a pure Ar gas was introduced to purge the sample for another 1 h. The FTIR spectrum of ethylbenzene adsorbed on the solid sample was then recorded. After that, the MnOₓ/CeO₂(0.05) catalyst was treated at 200 °C in O₂ for 1 h and then cooled to room temperature. Equivalently, ethylbenzene was introduced into the sample again and the FTIR spectrum was collected for understanding its adsorption behavior on the oxidized MnOₓ/CeO₂(0.05) sample. The chamber temperature was then increased to 80 °C with an oxygen flow and the FTIR spectra were recorded to characterize the interaction of ethylbenzene with the catalyst.

In-situ Raman spectroscopy
Raman spectra were recorded using an HR800 Raman spectrometer equipped with an Ar excitation source (λ = 514.532 nm). The gaseous steam was introduced into the system with a flow of Ar carrier gas (30 sccm) with the reactant partial pressure in the range of 10-20 mbar. To prove the presence of active surface oxygen species, in-situ Raman spectra were performed with 40 mg of the CeO₂ or MnOₓ/CeO₂(0.05) sample dried in a vacuum overnight to remove the water species. The Raman spectra of CeO₂ were recorded at room temperature in air. The Raman spectra of MnOₓ/CeO₂(0.05) were recorded at room temperature in air, room temperature in O₂, 140 °C in CO, 250 °C in CO, 350 °C in CO and 350 °C in CO and O₂.

To further confirm the active surface oxygen species, in-situ oxidation of CO was conducted with 40 mg of the CeO₂ or MnOₓ/CeO₂(0.05) sample dried in a vacuum overnight to remove the water species. The Raman spectra of CeO₂ were recorded at room temperature in air. The Raman spectra of MnOₓ/CeO₂(0.05) were recorded at room temperature in air, room temperature in O₂, 140 °C in CO, 250 °C in CO, 350 °C in CO and 350 °C in CO and O₂.

Catalytic data analysis
Carbon balance during oxidation of hydrocarbons
The carbon balance before and after the reaction was calculated based on the number of carbon atoms in all the liquid reactants and products. For example, in the oxidation of ethylbenzene, acetophenone and phenylethyl alcohol are the detectable liquid products, while the CO₂ from over-oxidation was not included in calculating the carbon balances. The carbon balance values are calculated according to the following equation:

\[ C\% = \frac{M_j n_j + M_1 n_1 + M_2 n_2 + M_3 n_3 + \ldots + M_x n_x}{M_e n_e} \times 100\% \]
where C% is the carbon balance, \( M_f \) is the final number of moles of ethylbenzene in the reactor after reaction, \( s \) is the number of carbon atoms in a single ethylbenzene molecule, \( M_i (M_{i1}, M_{i2}, \ldots, M_{ix}) \) is the number of moles of liquid product 1 (product 2, 3, \ldots, \( x \)) in the reactor after the reaction, \( n_i (n_{i1}, n_{i2}, \ldots, n_{ix}) \) is the number of carbon atoms in a single molecule of product 1 (product 2, 3, \ldots, \( x \)) and \( M_e \) is the number of moles of ethylbenzene in the feed mixture before the reaction.

In the kinetic study, the average reaction rates were calculated from the number of moles of substrate converted per gram of the catalyst in 1 h (mmol g\(^{-1}\) cat h\(^{-1}\)) and the conversion of the reactants was controlled to be lower than 20%, which approximated the true reaction rates.

**RESULTS AND DISCUSSION**

**Synthesis and structural characterization**

The CeO\(_2\) support was synthesized via a citric acid-assisted method [Figure 1A]. Typically, Ce(NO\(_3\))\(_3\) and citric acid were dissolved in a mixture of water, ethanol and glycerol, where the citric acid can chelate with metal ions to form the metal citrate precursor [Supplementary Figure 1]. After removing the solvent and forming a fluffy material by stirring at 90 °C, followed by calcination to remove the organic species, the CeO\(_2\) was finally obtained [Supplementary Figure 2]. The CeO\(_2\)-supported manganese oxide catalysts were synthesized following the same procedures by adding Mn(NO\(_3\))\(_2\) in the starting solution and denoted as MnO\(_x\)/CeO\(_2\)(\(y\)) [where \( y \) is the theoretical molar ratio of Mn/(Mn + Ce)] [Supplementary Figures 3-5].

Figure 1B shows the X-ray diffraction (XRD) patterns of the commercial CeO\(_2\) and MnO\(_x\)/CeO\(_2\)(\(y\)) samples with different Mn loadings, which all exhibit peaks at 28.7°, 33.3°, 47.7° and 56.5°, assigned to the (111), (200), (220) and (311) diffraction peaks of a typical CeO\(_2\) crystal, respectively\(^{[18,22]}\). Notably, the shift of these diffraction peaks was undetectable for the MnO\(_x\)/CeO\(_2\)(\(y\)) samples compared to the pure CeO\(_2\), suggesting a lack of the Mn-Ce solid-solution phase\(^{[18,22]}\). The high dispersion and/or amorphous features of MnO\(_x\) on the CeO\(_2\) matrix were evidenced by the undetectable XRD peaks associated with manganese oxide for MnO\(_x\)/CeO\(_2\)(0.025), MnO\(_x\)/CeO\(_2\)(0.05) and MnO\(_x\)/CeO\(_2\)(0.1) [Figure 1C]. However, the diffraction patterns of higher Mn content samples showed the crystallization of a Mn\(_3\)O\(_4\) hausmannite phase (JCPDS 071841)\(^{[28]}\), demonstrating the formation of sintered MnO\(_x\) species in these samples.

The N\(_2\) sorption demonstrates that the surface areas of CeO\(_2\) and MnO\(_x\)/CeO\(_2\)(0.05) are lower than 10 m\(^2\)/g, which should be due to the high-temperature calcination of the catalysts (800 °C for 4 h) that lead to the aggregation of the CeO\(_2\) support and the collapse of the pore structure. The surface geometry of MnO\(_x\)/CeO\(_2\)(0.05) was studied by electron microscopy characterization. As shown in Figure 2A, the bright field-scanning transmission electron microscopy image provides direct observation of the sample, showing stacked CeO\(_2\) crystals [Supplementary Figure 6]. The Mn distribution was identified by the energy dispersive spectroscopy (EDS) elemental maps [Figure 2B-D], showing the MnO\(_x\) ensembles with diameters of 15-25 nm on the CeO\(_2\) support, which is different from the Mn-Ce solid solution with homogeneously distributed Mn sites\(^{[18]}\), consistent with the XRD results [Figure 1B]. Interestingly, the morphology of the MnO\(_x\) ensemble is irregular, which might suggest the amorphous structure of the MnO\(_x\).

Figure 2E shows an enlarged view of the region in the yellow square in Figure 2A. Notably, the crystalline feature of the Mn species is completely unobservable. However, the elemental maps decidedly confirmed the existence of the MnO\(_x\) species [Figure 2F-H], demonstrating that the structural feature of MnO\(_x\)/CeO\(_2\)(0.05) is mainly amorphous MnO\(_x\) on the surface of the CeO\(_2\) matrix. The annular bright field-scanning transmission electron microscopy image with atomic resolution clearly shows the distributions of the Ce, O and Mn elements. As shown in Figure 2I-L, the ordered distributions of Ce and O are the same as
Figure 1. (A) Procedures for synthesizing MnOₓ/CeO₂(y) catalyst with MnOₓ species anchored on the surface of ceria matrix. (B) XRD patterns of commercial CeO₂ and MnOₓ/CeO₂(y) catalysts with different Mn loadings. (C) Zoomed-in views of diffractions peaks in (A) from 30° to 40° for MnOₓ/CeO₂(y) catalysts with different Mn loadings. (D) O1s X-ray photoelectron spectra of MnOₓ/CeO₂(0.05), CeO₂, and MnO₂. XRD: X-ray diffraction.

those of the CeO₂ lattice. However, the random distribution of Mn confirms the amorphous feature of the MnOₓ species. Significantly, the formation of an Mn-Ce solid solution is also excluded, because the smaller ionic radius of manganese ions compared to cerium ions will result in contractive lattice space in the Mn-Ce solid solution compared to the lattice space of CeO₂[18].

The high-resolution HAADF-STEM image of the MnOₓ/CeO₂(0.05) catalyst directly shows that the CeO₂ matrix is partially coated with layers with an undetectable lattice [Figure 2M]. In particular, in this case, the catalyst calcined at 800 °C for 4 h precluded the carbon-containing species on the surface of CeO₂. Considering that isolated Ce sites can be found in the amorphous region [Figure 2N], it is reasonable to assign the amorphous layers to the MnOₓ species. In addition, the Mn/(Mn + Ce) ratio appears at 0.22 on the catalyst surface by XPS analysis, which is distinctly different from the ratio of 0.05 in the whole oxides, indicating that MnOₓ mainly exists on the CeO₂ surface. These results suggest that the structural feature of MnOₓ/CeO₂(0.05) is dominated by amorphous MnOₓ layers on the surface of the CeO₂ matrix rather than a monophasic solid solution. The unique structure of MnOₓ/CeO₂(0.05) can be reasonably assigned to the citric acid-assisted method [Figure 1A], because the remarkably different decomposition temperature of cerium citrate (~161 °C) and manganese citrate (~296 °C) would benefit the phase separation to hinder the formation of the solid solution.

The MnOₓ structure was further characterized by Raman and EPR measurements. As shown in Figure 2O and Supplementary Figure 7, the as-synthesized MnOₓ/CeO₂(0.05) catalyst shows a blue shift of the MnOₓ mode (654 cm⁻¹) compared with that of various manganese oxide and supported MnOₓ catalysts prepared by the conventional impregnation method (≤ 640 cm⁻¹), which is due to the SOSIs between MnOₓ and the CeO₂ support and the formation of defect-rich MnOₓ layers[29-31]. In contrast, the EPR spectrum of the MnOₓ
Figure 2. Electron microscopy and structural characterization. (A, E) BF-STEM images and the corresponding (B-D, F-H) Mn, Ce and O elemental maps of MnO\textsubscript{x}/CeO\textsubscript{2}(0.05). (E) Enlarged view of the yellow square in (A). (I-L) ABF-STEM and EDS analysis of MnO\textsubscript{x}/CeO\textsubscript{2}(0.05). (M, N) High-resolution STEM images of MnO\textsubscript{x}/CeO\textsubscript{2}(0.05) catalyst. The isolated Ce sites in the amorphous region are highlighted by yellow circles in (N). (O) Raman and (P) EPR spectra of various samples. BF-STEM: Bright field-scanning transmission electron microscopy; ABF-STEM: annular bright field-scanning transmission electron microscopy.

MnO\textsubscript{x}/CeO\textsubscript{2}(0.05) catalyst shows sharp sextuple signals with a g value at 2.00 [Figure 2P], indicating the formation of abundant oxygen vacancies by loading of the MnO\textsubscript{x} species in the MnO\textsubscript{x}/CeO\textsubscript{2}(0.05) catalyst\textsuperscript{32}. For comparison, the bulky manganese oxide (MnO\textsubscript{2}), MnO\textsubscript{x}/CeO\textsubscript{2} and MnO\textsubscript{x}/SiO\textsubscript{2} prepared by the conventional impregnation method [Supplementary Figure 8] exhibit broad and weak signals in the EPR spectra [Figure 2P], which can be attributed to the Mn-Mn coupling (i.e., aggregation\textsuperscript{33-35}). These results reasonably confirmed the successful formation of well-dispersed and amorphous MnO\textsubscript{x} layers on the surface of the ceria matrix and the construction of abundant oxygen vacancies/defective sites in the MnO\textsubscript{x}/CeO\textsubscript{2}(0.05) catalyst, which are beneficial for the oxygen activation.

Figure 1D shows the O1s X-ray photoelectron spectra of the MnO\textsubscript{x}/CeO\textsubscript{2}(0.05), CeO\textsubscript{2} and MnO\textsubscript{2} samples. All samples show three peaks at 529.3, 531.4 and 532.7 eV, which can be assigned to the lattice oxygen of O\textsuperscript{2-} (O\textsubscript{lat}), surface oxygen of O\textsuperscript{2-}, O\textsuperscript{22-} or O\textsuperscript{2-} (O\textsubscript{sur}) and adsorbed oxygen species from water/carbonate on the solid surface (O\textsubscript{ads}), respectively\textsuperscript{18,19,28}. In these multiple oxygen species, the surface oxygen species from the defective site with an unsaturated structure displays a key role in the oxidation, which is denoted as active oxygen\textsuperscript{18,26}. The atomic ratio of active oxygen to the total oxygen atoms on the oxide surface of CeO\textsubscript{2} and MnO\textsubscript{2} is 26.8% and 28.4%, respectively, while the MnO\textsubscript{x}/CeO\textsubscript{2}(0.05) exhibited a remarkably improved active oxygen capacity of 46.1% [Supplementary Table 1], which is even comparable to that of Mn-Ce solid solutions (44.1%) with a high Mn loading (50%)\textsuperscript{18}. Considering that the MnO\textsubscript{x}/CeO\textsubscript{2}(0.05) has a low Mn loading (5%) and is mainly presented as amorphous MnO\textsubscript{x} layers on the CeO\textsubscript{2} surface, the high capacity of
active oxygen should be due to the maximized interfacial effect, causing the rich Ce\(^{4+}\) and Mn\(^{2+}/\)Mn\(^{3+}\) species [Supplementary Table 1, Figure 2P, Supplementary Figure 9] on the surface to benefit the formation of unsaturated oxygen.

**Redox investigation**

The redox properties of the active oxygen species on MnO\(_x\)/CeO\(_2\)\((0.05)\) were firstly identified by the O1s X-ray photoelectron spectrum in a temperature-programmed redox cycle [Figure 3A, Supplementary Figure 10, Supplementary Table 2]. Hydrogen treatments at low temperature (room temperature to 80 °C) partially reduced the surface oxygen sites, as evidenced by the decreased intensity of the O1s peak of O\(_{\text{ads}}\) (531.4 eV) (Figure 3A and its inset), indicating that active oxygen species were available at low temperature. The subsequent reduction at the higher temperature of 120 °C led to further removal of the active oxygen. Very importantly, the active oxygen can be regenerated after treatment in air at 50 °C, displaying a similar O1s X-ray photoelectron spectrum to that of the as-synthesized sample (Figure 3A and its inset). Therefore, the high activity and remarkable stability of MnO\(_x\)/CeO\(_2\)\((0.05)\) in the catalytic oxidation at low temperatures are reasonably expected.

Further evidence regarding the redox properties of the active oxygen species is provided by *in-situ* Raman spectroscopy. As shown in Supplementary Figure 11, MnO\(_x\)/CeO\(_2\)\((0.05)\) gives the F\(_2g\) mode of the CeO\(_2\) matrix at 460 cm\(^{-1}\) [23,30,36]. Compared to the spectrum of CeO\(_2\), MnO\(_x\)/CeO\(_2\)\((0.05)\) shows an additional band at 656 cm\(^{-1}\) [Figure 3B], which is associated with the Mn-O-Mn stretching mode of the surface amorphous MnO\(_x\) species with abundant defects [29-31], corresponding to the active oxygen in the X-ray photoelectron spectra [Figure 3A]. Notably, broadening, a decrease in intensity and a red shift of the band at 656 cm\(^{-1}\) occurred during the *in-situ* treatment of MnO\(_x\)/CeO\(_2\)\((0.05)\) in atmospheric Ar at 140 °C. The intensity of the band at 645 cm\(^{-1}\) was further decreased when the temperature increased to 250 and 350 °C in Ar. This can be well explained by the desorption of the active oxygen species associated with MnO\(_x\) species to form Mn sites with more defects [20,23]. Considering the well-dispersed, amorphous and layered structure of the MnO\(_x\) species, it can be reasonably inferred that the desorption of the interfacial oxygen species accounts for the signal changes. To probe the reversibility of the active oxygen at low temperature, we exposed the sample to molecular oxygen at room temperature, resulting in a very similar Raman spectrum to the as-synthesized MnO\(_x\)/CeO\(_2\)\((0.05)\) sample, thereby confirming the reversibility of active oxygen species [Figure 3B, Supplementary Figure 12], in good agreement with the *in-situ* XPS results [Figure 3A]. The active oxygen on MnO\(_x\)/CeO\(_2\)\((0.05)\) was further evidenced by the O\(_2\)-TPD test [Supplementary Figure 13]. The active and reproducible oxygen species over MnO\(_x\)/CeO\(_2\)\((0.05)\) make it a potentially efficient catalyst for aerobic oxidation reactions.

In order to support this conclusion, we further evaluated the catalytic performance of the MnO\(_x\)/CeO\(_2\)\((0.05)\) catalyst for the CO oxidation reaction, where the activation of oxygen molecules is regarded as a key step [37-38]. Figure 4A shows the dependence of CO conversion on temperature over the MnO\(_x\)/CeO\(_2\)\((0.05)\) and CeO\(_2\) catalysts. The positive role of the interfacial effect on MnO\(_x\)/CeO\(_2\)\((0.05)\) is evidenced by the full conversion of CO over MnO\(_x\)/CeO\(_2\)\((0.05)\) at a lower temperature (270 °C) than that over CeO\(_2\) (370 °C). By correlating the inverse of the absolute temperature (1/T) with the initial reaction rates, the apparent activation energies of MnO\(_x\)/CeO\(_2\)\((0.05)\) and CeO\(_2\) appeared at 51.4 and 69.2 kJ/mol, respectively [Figure 4B]. The relatively lower apparent activation energy of MnO\(_x\)/CeO\(_2\)\((0.05)\) indicates that CO oxidation is easier. Based on the understanding that the activation energy is sensitive to the different active oxygen [37,39], a lower apparent activation energy of MnO\(_x\)/CeO\(_2\)\((0.05)\) than that of CeO\(_2\) should be reasonably attributed to the abundant Mn-O-Ce interfacial sites to activate O\(_2\), rather than simply increasing the number of active oxygen species. Figure 4C shows the dependence of the reaction rate on oxygen partial pressure over different catalysts, where MnO\(_x\)/CeO\(_2\)\((0.05)\) always displays higher reaction rates than CeO\(_2\) at
Figure 3. Redox study. (A) In-situ O1s X-ray photoelectron spectra of MnOx/CeO2(0.05) under different redox conditions. Inset: the dependences of O$_{\text{sur}}$ capacities on redox conditions. (B) In-situ Raman spectra of MnOx/CeO2(0.05) and CeO2 under different conditions.

the same oxygen pressure, thereby demonstrating its higher activities. Interestingly, under relatively low oxygen pressure (1.0-3.5 kPa), the reaction rates ($r_o$) over CeO2 increased constantly with oxygen pressure, showing the reaction kinetic order at 0.37 [Figure 4D]. In contrast, the influence of oxygen pressure on the $r_o$ of MnOx/CeO2(0.05) is minimal with a kinetic order at 0.04 [Figure 4D]. A lower reaction kinetic order suggests that the activity of MnOx/CeO2(0.05) is insensitive to the oxygen pressure[37,40], which is reasonably attributed to the enhanced ability of the well-dispersed and amorphous MnOx species in MnOx/CeO2(0.05) to activate molecular oxygen efficiently. These results indicate that the proof-of-concept design of the catalyst benefits the enhancement of catalytic efficacy in aerobic oxidations.

Aerobic oxidation of hydrocarbons
Initial attempts to evaluate the catalysts were performed in the selective oxidation of ethylbenzene to acetophenone and 1-phenylethanol at a low temperature of 110 °C for 6 h without solvent and initiator additives [Table 1]. A higher molar ratio of acetophenone and 1-phenylethanol indicates the deep dehydrogenation of 1-phenylethanol to acetophenone. The blank run without catalysts showed undetected reactivity (entry 1). The commercial nanosized CeO2, MnO2 and CeO2 were active for the reaction, giving ethylbenzene conversion at 3.0%, 1.3% and 6.8%, respectively (entries 2-4). The Mn salts of MnCl2 and KMnO4, which are well-known homogeneous catalysts in oxidation, gave ethylbenzene conversion at 8.2% and 1.9%, respectively (entries 5 and 6). Interestingly, interfacing MnOx on CeO2 significantly influenced the catalytic activity, where enhanced conversions were achieved over the MnOx/CeO2 catalysts (entries 7-11). By optimizing the Mn loadings on the catalysts, the best performance was achieved over MnOx/CeO2(0.05) with the highest capacity of active surface oxygen, displaying ethylbenzene conversion at 12.9% (entry 8). The decreased activity for the MnOx/CeO2 catalysts with an Mn/(Mn + Ce) ratio higher than 0.05 is due to the aggregation of the MnOx species [Figure 1C], leading to limited Mn-O-Ce interfacial sites for the oxidation of substrates. Very interestingly, the oxidation of ethylbenzene can be performed at a low temperature at 70 °C (entry 14), demonstrating the superior catalytic activity of MnOx/CeO2(0.05).
To realize the best performance, we optimized the reaction temperature, time, catalyst amount and oxygen pressure in the reactor (entries 12-21). The ethylbenzene conversion of 59.2% with > 99.0% selectivity to acetophenone and 1-phenylethanol was achieved (entry 19). This result, obtained under solvent- and initiator-free conditions, even outperforms a series of superior catalysts for C-H bond selective oxidations reported in the literature [Supplementary Table 3], such as the Au nanosheet with undetectable reactivity under solvent- and initiator-free conditions[12]. The MnO$_x$/CeO$_2$ catalyst synthesized from the conventional impregnation method with the same Mn loading to MnO$_x$/CeO$_2$(0.05) exhibited poor activity (entry 22), which might be due to the aggregation of the MnO$_x$ particles and the limited interfacial sites, as confirmed by the Raman and EPR analysis [Figure 2O and P]. Increasing the MnO$_x$/CeO$_2$(0.05) catalyst amount led to enhanced ethylbenzene conversion but unsatisfactory carbon balance values because of the over-oxidation to CO and CO$_2$ (entries 20 and 21, Supplementary Figure 14). The molecular oxygen indeed acted as oxygen donors in the reaction, as evidenced by the undetectable conversion of ethylbenzene when using nitrogen instead of oxygen in the reaction (entry 23). When the free radical scavenger was added to the reaction system, the reaction was quenched, demonstrating that the reaction follows a radical chain mechanism (entry 24).

More importantly, the catalyst is stable, reusable and can be easily filtrated and recycled after each reaction run. Consequently, it exhibited stable catalytic performance in the recycling tests.

Table 1. Catalytic data in oxidation of ethylbenzene$^a$

| Entry | Catalyst | Temp. (°C) | Time (h) | Conv. (%) | Sel. (%) | A/P$^b$ |
|-------|----------|------------|----------|-----------|----------|--------|
| 1     | Blank    | 110.0      | 6.0      | < 0.1     | n.d.     | n.d.   |
| 2     | Commercial CeO$_2$ | 110.0 | 6.0 | 3.0 | > 99.0 | 0.8 |
| 3     | MnO$_2$  | 110.0      | 6.0      | 1.3       | > 99.0   | 0.6    |
| 4     | CeO$_2$  | 110.0      | 6.0      | 6.8       | > 99.0   | 1.1    |
| 5$^c$ | MnCl$_2$ | 110.0      | 6.0      | 8.2       | 97.6     | 2.6    |
| 6$^c$ | KMnO$_4$ | 110.0      | 6.0      | 1.9       | 94.7     | 2.0    |
| 7     | MnO$_x$/CeO$_2$(0.025) | 110.0 | 6.0 | 9.2 | > 99.0 | 1.2 |
| 8     | MnO$_x$/CeO$_2$(0.05) | 110.0 | 6.0 | 12.9 | > 99.0 | 1.9 |
| 9     | MnO$_x$/CeO$_2$(0.1) | 110.0 | 6.0 | 5.6 | > 99.0 | 0.4 |
| 10    | MnO$_x$/CeO$_2$(0.2) | 110.0 | 6.0 | 4.1 | > 99.0 | 0.5 |
| 11    | MnO$_x$/CeO$_2$(0.3) | 110.0 | 6.0 | 27.1 | > 99.0 | 2.1 |
| 12    | MnO$_x$/CeO$_2$(0.05) | 110.0 | 6.0 | 29.4 | > 99.0 | 2.6 |
| 13    | MnO$_x$/CeO$_2$(0.05) | 110.0 | 6.0 | 9.2 | > 99.0 | 0.8 |
| 14    | MnO$_x$/CeO$_2$(0.05) | 110.0 | 6.0 | 4.3 | > 99.0 | 1.5 |
| 15    | MnO$_x$/CeO$_2$(0.05) | 110.0 | 6.0 | 24.2 | > 99.0 | 2.0 |
| 16    | MnO$_x$/CeO$_2$(0.05) | 110.0 | 6.0 | 34.7 | > 99.0 | 1.9 |
| 17    | MnO$_x$/CeO$_2$(0.05), 200 mg | 110.0 | 6.0 | 52.8 | > 99.0 | 3.4 |
| 18    | MnO$_x$/CeO$_2$(0.05), 400 mg | 110.0 | 6.0 | 59.2 | > 99.0 | 7.0 |
| 19    | MnO$_x$/CeO$_2$(0.05), 400 mg, 3 MPa of O$_2$ | 110.0 | 6.0 | 63.5 | 95.7 | 5.8 |
| 20    | MnO$_x$/CeO$_2$(0.05), 600 mg, 3 MPa of O$_2$ | 110.0 | 6.0 | 65.6 | 77.6 | 4.7 |
| 21    | MnO$_x$/CeO$_2$(0.05), 2 MPa of N$_2$ | 110.0 | 6.0 | 19.2 | > 99.0 | 16 |
| 22$^d$ | MnO$_x$/CeO$_2$ | 110.0 | 6.0 | < 0.1 | n.d. | n.d. |
| 23    | MnO$_x$/CeO$_2$(0.05), 50 mg of hydroquinone | 110.0 | 6.0 | < 0.1 | n.d. | n.d. |

$^a$Reaction conditions: 47 mmol of substrate, 100 mg of catalyst, 2.0 MPa of oxygen; $^b$A/P: molar ratio of acetophenone and 1-phenylethanol; $^c$Molar weight of the Mn in the catalyst is the same as the molar weight of Mn in MnO$_x$/CeO$_2$(0.05); $^d$Catalyst prepared from conventional impregnation method. Conv.: Conversion; Sel.: selectivity to acetophenone and 1-phenylethanol; n.d.: not detected.
Figure 4. CO oxidation. (A) Dependence of CO conversion on temperature over MnO$_x$/CeO$_2$(0.05) and CeO$_2$ catalysts. (B) Arrhenius plots of CO oxidation over MnO$_x$/CeO$_2$(0.05) and CeO$_2$ catalysts. (C) Dependence of reaction rate on oxygen pressure in CO oxidation over MnO$_x$/CeO$_2$(0.05) and CeO$_2$ catalysts. (D) Data characterizing the kinetic reaction order of oxygen in CO oxidation over MnO$_x$/CeO$_2$(0.05) and CeO$_2$ catalysts.

[Supplementary Figure 15]. In the six runs of selective ethylbenzene oxidation, the MnO$_x$/CeO$_2$(0.05) catalyst exhibited constant conversion and selectivity, indicating good recyclability and stability. Notably, the MnO$_x$/CeO$_2$(0.05) catalyst is generally effective for the selective oxidation of various phenolic hydrocarbons [Supplementary Table 4], giving desired products with good activities and selectivities. It is noteworthy that these reactions were all performed under solvent- and initiator-free conditions, which make the MnO$_x$/CeO$_2$(0.05) catalyst potentially useful for wide applications in the selective oxidation of C-H bonds.

Mechanism investigation

Based on the aforementioned results, we conclude that MnO$_x$/CeO$_2$(0.05) is highly active for the selective oxidation of C-H bonds under solvent- and initiator-free conditions at low temperature based on its earth-abundant metals as catalysts and constructing SOSIs. In contrast to the existing understanding that highly active Mn-Ce catalysts should be dominated by the solid-solution phase, the greatest difference in our case is that MnO$_x$/CeO$_2$(0.05) has separated phases of two-dimensional and amorphous MnO$_x$ layers on CeO$_2$. We conclude that the high efficacy of MnO$_x$/CeO$_2$(0.05) originates from the SOSIs and maximized interfacial effects, because a highly active solid-solution catalyst requires a high Mn concentration (~50%)\cite{18}.

In order to further address this conclusion, we performed acid treatment for MnO$_x$/CeO$_2$(0.05) to partially remove the surface MnO$_x$ species, as confirmed by the X-ray photoelectron spectra giving the surface Mn/(Mn + Ce) ratio decreased from 0.22 to almost undetectable [Figure 5A]. The acid-treated
MnO/\(\text{CeO}_2\) (0.05) exhibited a significantly reduced ethylbenzene conversion rate (8 mmol g\(^{-1}\) h\(^{-1}\)) compared to the fresh catalyst (28 mmol g\(^{-1}\) h\(^{-1}\)) [Figure 5B] under equivalent reaction conditions, demonstrating the important role of the surface MnO\(_x\) species of MnO\(_x\)/\(\text{CeO}_2\) (0.05) in generating abundant interfacial active sites. In order to understand the role of active oxygen on MnO\(_x\)/\(\text{CeO}_2\) (0.05) for C-H bond oxidation, we performed in-situ FTIR spectroscopy studies of C-H bond oxidation. Figure 5C shows the ethylbenzene-adsorption FTIR spectrum of MnO\(_x\)/\(\text{CeO}_2\) (0.05), which gives the typical peak at 1450 cm\(^{-1}\) assigned to the C-H bond\(^{[18]}\). By increasing the temperature to 160 °C in flowing Ar, the C-H peak was remarkably weakened, which should be due to the activation of the C-H bond by the surface oxygen species on the MnO\(_x\)/\(\text{CeO}_2\) (0.05) catalyst, because the hydrocarbon favors reacting with the active surface oxygen with an asymmetric Coulombic interaction with Mn and Ce\(^{[18,20]}\). Meanwhile, the readily observed C=O bond at 1641 cm\(^{-1}\) confirmed that the C-H bonds are indeed oxidized by the active oxygen on the solid surface into C=O species\(^{[18]}\). The introduction of external molecular oxygen further enhanced the transformation of the C-H bonds at 160 °C, as evidenced by the increased intensity of the C=O peak at 1641 cm\(^{-1}\).
The aforementioned results demonstrate the important role of the active oxygen species on the MnO$_x$/CeO$_2$(0.05) catalyst in activating C-H bonds. After purging MnO$_x$/CeO$_2$(0.05) with hydrogen to reduce the active oxygen at 200 °C, the system was switched to the Ar flow with ethylbenzene molecules at 25 °C. The reduced MnO$_x$/CeO$_2$(0.05) failed to adsorb ethylbenzene, as confirmed by the undetectable peak of C-H bonds in the in-situ FTIR spectrum [Figure 5D]. Furthermore, after regeneration of the active oxygen, the adsorption of C-H bonds occurred again on the regenerated catalyst at 25 °C. Increasing the temperature to 80 °C led to a significant weakening of the C-H bonds, confirming that they were readily activated by the regenerated active oxygen species. These phenomena demonstrate the important role of active oxygen in the adsorption and activation of C-H bonds.

CONCLUSIONS
In summary, we have demonstrated a ceria-supported two-dimensional manganese oxide with a SOSI effect as an efficient catalyst for the selective oxidation of hydrocarbons, thereby breaking the normal principle of synthesizing Mn-Ce catalysts with an abundant solid-solution phase. The key to the success is to anchor well-dispersed and amorphous MnO$_x$ layers on the CeO$_2$ matrix by SOSIs, forming abundant active oxygen species over MnO$_x$/CeO$_2$(0.05) because of the high interfacial efficacy, which displays crucial roles in the adsorption and activation of C-H bonds. In the selective oxidation of hydrocarbons to the corresponding alcohols and ketones, MnO$_x$/CeO$_2$(0.05) exhibited high activity, selectivity and recyclability under solvent- and initiator-free conditions at low temperature, outperforming the noble catalysts and the state-of-the-art Mn-Ce metal oxide catalysts. This work not only highlights the importance of SOSIs for the oxidation of C-H bonds but also extends the principle for designing efficient metal oxide catalysts for the sustainable production of valuable chemicals.

DECLARATIONS
Authors’ contributions
Carried out the catalyst preparation, characterization, catalytic tests, and prepared the draft manuscript: Wang H
Performed part of the catalyst characterization: Luo Q, Zhang J, Wang C
Performed the TEM characterization: Ge X, Zhang W
Planned the study, analysed the data and wrote the manuscript: Wang L, Xiao FS

Availability of data and materials
Not applicable.

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Conflict of interest
All authors declared that there are no conflicts of interest.

Ethical approval and consent to participate
Not applicable.
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