Template and interfacial reaction engaged synthesis of CeMnOₓ hollow nanospheres and their performance for toluene oxidation†

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A series of well-dispersed CeMnOₓ hollow nanospheres with uniform diameter and thickness were synthesized by a novel approach combining the template method and interfacial reaction. A SiO₂ template was used as a hard template for preparation of SiO₂@CeO₂ nanospheres by solvothermal reaction. SiO₂@CeMnOₓ could be formed after KMnO₄ was reacted with SiO₂@CeO₂ by interfacial reaction between MnO₂⁻ and Ce³⁺. Among all the prepared catalysts, CeMnOₓ-3 with a moderate content of Mn (15 wt%) exhibited the lowest temperature for complete combustion of toluene (280 °C). Moreover, it showed high stability for 36 h with toluene conversion above 97.7% and good water tolerance with 5 vol% H₂O. With characterization, we found that the reaction between Ce and Mn in the Ce–Mn binary oxides gave rise to increased Ce³⁺ and oxygen vacancies, which led to the formation of enhanced reducibility and more surface-absorbed oxygens (O₂²⁻, O²⁻ and O⁻), and improved the catalytic performance further.

1 Introduction

As one of the primary sources of air pollutants, volatile organic compounds (VOCs) are not only significant contributors to smog formation, but also can cause environmental pollution and bring great negative effects to human health.1,4 Some VOCs have been classified as carcinogens, such as benzene, toluene, dichloromethane, and dichloroethane. Therefore, the effective removal of VOCs has been an important research topic in environmental governance.

Numerous methods have been used to eliminate VOCs, including incineration, absorption, adsorption, condensation, and catalytic oxidation.4–7 Among them, catalytic oxidation has been recognized as one of the most effective and economical ways for abating VOCs, as it has the advantages of low degradation temperature, high removal efficiency, and no secondary pollution.4–7 To realize the industrial application of catalytic oxidation, the catalysts need to be developed extensively. So far, two types of traditional catalysts were researched deeply, including supported noble metals (such as Au, Pd, and Pt)4–9 and transition metal oxides.10,11 Although the former exhibits high activity and CO₂ selectivity at low temperatures, the high cost and high sensitivity to water vapor, sulfur and chlorine compounds limit their applications. Transition metal oxides, such as Co₃O₄,11,12 NiO,13 MnOₓ,14 CuO,15 and their composite oxides,16–18 possess the advantages of low cost and high toxicity resistance. However, the reaction temperature for these catalysts is relatively high, which will affect their stability and increase energy costs.

In addition to these two types of catalysts, CeO₂ is also reported as an effective catalyst for the catalytic oxidation of VOCs as it has high oxygen storage capacity caused by its excellent redox properties. In recent years, CeO₂ with different morphologies and structures was researched for VOCs oxidation.19,20 The catalytic activity of CeO₂ in the VOCs oxidation process can be improved by adding other elements to form composites, such as Mn, Cu, Ni and Co. The increment in catalytic performance may originate from the synergistic effect between CeO₂ and other metal oxides. The oxygen vacancy due to different electric states between Ce⁴⁺ and Mn⁷⁺ is another essential factor for the enhanced activity.16,21 Thereinto, Ce–Mn composite oxides with tunable structure and size have been often used for VOCs oxidation because of the low costs, improved catalytic performances, and high thermal stability. For example, Wang et al. synthesized CeO₂–MnOₓ and proved that the synergistic effect between Mn and Ce is the decisive factor on its excellent activity for benzene oxidation.22 Zhao et al. prepared a series of CeₓMnO₃ microspheres with arbutus-like hierarchical structure by coprecipitation. The Ce₀.03MnO₃ microspheres...
showed best catalytic activity for toluene oxidation with high stability and water resistance, due to the Mn\(^{3+}\) species and abundant surface oxygen.\(^{24}\) As 3D nano/micro-structured materials (including hollow nanospheres) possess high surface area and low density, they exhibit some advantages superior to corresponding bulk materials, which are beneficial for their application in catalysis, drug delivery, supercapacitors and so on.\(^{25-27}\) Although little progress has been made in terms of synthesis and catalytic performance of CeO\(_2\)-MnO\(_x\) hollow nanospheres, the as-obtained materials could not possess homogeneous structure, including uniform morphology, diameter, and interior architecture.\(^{28,29}\) In this paper, we prepared well-defined CeMnO\(_x\) hollow nanospheres with different amounts of MnO\(_x\) by the combination of template method and interfacial reaction. Toluene was chosen as the target contaminant for catalytic oxidation. By tuning the content of MnO\(_x\) in the catalysts, the effect of Ce/Mn ratio on catalytic activity was evaluated. Our results demonstrated that CeMnO\(_x\)-3 with moderate content of Mn (15 wt\%) showed low temperature for complete combustion of toluene (280 °C) and high stability for 36 h with toluene conversion above 97.7%. It also exhibited good water tolerance and recyclability under the condition of 5 vol% H\(_2\)O. Based on the study of catalysts, including structure, morphology, element states, and catalytic performance, the synergistic effect between Ce and Mn was proposed to play a critical role in the improvement of catalytic performance.

2 Experimental

The detailed Experimental section is described in the ESI.†

3 Results and discussion

3.1 Composition and structure

XRD was conducted to characterize the crystalline structures of as-prepared catalysts. As displayed in Fig. 1, the peaks for all the samples are similar and could be indexed to fluorite CeO\(_2\) (JCPDS no. 34-0394) and no diffraction peak of MnO\(_x\) species is observed. Meanwhile, compared with the prominent reflection peaks (111 and 220) of CeO\(_2\), a slight shift to higher Bragg angles is observed for the CeMnO\(_x\) binary oxides. For the radius of Mn\(^{3+}\) (0.064 nm) and Mn\(^{4+}\) (0.060 nm) are smaller than those of Ce\(^{3+}\) (0.134 nm) and Ce\(^{4+}\) (0.114 nm), the spacing between crystal planes (d) of CeO\(_2\) decreased when the manganese ions substituted cerium ions. Therefore, the value of \(\theta\) for CeMnO\(_x\) is calculated to be higher than that of CeO\(_2\) from Bragg’s law: 2\(d\) sin \(\theta\) = \(k\lambda\).\(^{30}\) This shift also illustrates that Mn has successfully migrated into the CeO\(_2\) lattice through interfacial reaction due to the close contact between Ce\(^{5+}\) and Mn\(^{4+}\) during the calcination process. The introduction of Mn species could modify the crystallization of CeO\(_2\), and form Mn–Ce solid solution. The difference in ionic radius means that the defects in the CeO\(_2\) lattice are easily formed, including oxygen vacancies that can provide active centers for the creation of reactive oxygen species.\(^{31}\)

The synthesis process of CeMnO\(_x\) composite included three main steps and was illustrated in Scheme 1. Firstly, homogeneous SiO\(_2@\)CeO\(_2\) was synthesized by the solvothermal method.\(^{32-34}\) In this step, uniform SiO\(_2\) spheres with a diameter of about 250 nm (Fig. S1 in the ESI†) were used as templates, and CeO\(_2\) nanoparticles were covered on the surface of SiO\(_2\) spheres by the self-assembly method. From XRD in Fig. S2,† we can see that the nanoparticles on SiO\(_2\) were CeO\(_2\) even though the broad diffraction peaks illustrate its low crystallinity, indicating CeO\(_2\) could be obtained just after the solvothermal treatment of Ce(NO\(_3\))\(_3\) directly. In the second step, SiO\(_2@\)CeO\(_2\) was dispersed in KMnO\(_4\) solution to coat the MnO\(_x\) layer. Although most of Ce in SiO\(_2@\)CeO\(_2\) existed in the form of Ce\(^{4+}\) with high valence, there was still a small amount of Ce\(^{3+}\) coming from the transformation of Ce\(^{5+}\) due to the excellent redox behavior of CeO\(_2\). KMnO\(_4\) with strong oxidation ability would oxidize this tiny amount of Ce\(^{3+}\) to CeO\(_2\) and be reduced to MnO\(_x\) itself. This reaction can also be indirectly observed by the color change of the reaction system from purple to dark brown, corresponding to the color of MnO\(_x\) and MnO\(_2\), respectively. In addition, the rough surface formed by the accumulation of CeO\(_2\) nanoparticles in the first step could increase the contact between KMnO\(_4\) and Ce(nitrate) and accelerate the surface interaction. At last, the SiO\(_2\) core was etched with NaOH solution and CeMnO\(_x\) hollow spheres were obtained.

ICP-AES was used to ascertain the amount of Mn in the CeMnO\(_x\) catalysts. The actual contents of Mn in CeMnO\(_x\) catalysts increase with the concentration of KMnO\(_4\) solution. It should be noticed that the preparation method involves the

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Fig. 1 XRD patterns of CeO\(_2\) and the as-prepared CeMnO\(_x\) hollow sphere catalysts.

Scheme 1 Schematic illustration for the preparation of CeMnO\(_x\) hollow spheres.
oxidation of Ce$^{3+}$ on the surface of CeO$_2$ with KMnO$_4$ to obtain MnO$_x$. As the amount of Ce$^{3+}$ in CeO$_2$ is fixed, the content of MnO$_x$ reaches saturation for CeMnO$_x$-4 (19.0%), which is close to sample 5, 18.90%.

Raman spectra of catalysts CeO$_2$ and the CeMnO$_x$ are shown in Fig. 2. The band at 460 cm$^{-1}$ is assigned to the triply degenerated F$_{2g}$ active mode of CeO$_2$, which reflects the symmetric breathing pattern of oxygen atoms around cerium ions in the fluorite CeO$_2$. With the increase of Mn contents, the F$_{2g}$ band shifts to lower wavenumbers (red shift) gradually, suggesting the variations of Ce–O bonding symmetry. The red shifts may attribute to the lattice contraction and consequent oxygen vacancies, which both originated from the partial incorporation of Mn ions with smaller radius into fluorite CeO$_2$. No Raman peaks for MnO$_x$ species (e.g. Mn$_3$O$_4$) could be observed in the CeMnO$_x$ catalysts, which reveals that the MnO$_x$ in the binary oxides is highly dispersed, in accordance with XRD results.

N$_2$ adsorption–desorption isotherms of CeO$_2$ and CeMnO$_x$ are displayed in Fig. 3. All the catalysts present type II isotherms with H3-type hysteresis loops. According to IUPAC classification, these isotherms suggest the presence of slit-shaped micropores in the samples. The Brunauer–Emmett–Teller (BET) surface areas of the catalysts in Table 1 show an obvious downtrend (from 107.2 to 23.8 m$^2$ g$^{-1}$) opposite to that of Mn content, indicating the addition of Mn leads to a more compact structure, which could be confirmed by SEM images in the following section.

As CeMnO$_x$-3 exhibited the best catalytic activity among all the CeMnO$_x$ catalysts, it was chosen as an example to study the morphologies by SEM and the images of other samples were given in Fig. S3†. The SiO$_2$@[CeMnO$_x$]-3 before NaOH treatment are composed of large-scale uniform and well-dispersed microspheres with 250–400 nm in diameter (Fig. 4a). The surfaces of the microspheres are rough and consists of small particles, indicating that CeO$_2$ nanoparticles has deposited on the SiO$_2$ templates successfully. After removing of SiO$_2$ templates with NaOH treatment, CeMnO$_x$-3 hollow spheres can be obtained (Fig. 4b), which inherit the morphologies of their precursors well. A few cracked spheres in Fig. 4b and c reveal their hollow features clearly. A high magnified SEM image of a ruptured CeMnO$_x$-3 microsphere in Fig. 4d reveals that the thickness of the hollow sphere is about 50 nm and the sphere is composed of abundant nanoparticles, contributing to a high specific surface area. For SiO$_2$@[CeO$_2$] before NaOH treatment, the surfaces were composed of nanoparticles with 20 nm in diameter (Fig. S3a†). With careful observation, we can see that the SiO$_2$@[CeO$_2$] nanospheres are loosely structured, with some areas showing a tendency to delaminate, indicating the weak interaction between the nanoparticles. For this reason, the shells of CeO$_2$ hollow sphere are fragile and easily to be broken after NaOH treatment, which is indicated by many broken spheres in Fig. S3b.† With the increase of Mn content, the ratio of broken spheres decreases and the surface of the spheres gets smoother and more compact, indicating the interaction between nanoparticles is enhanced, which is also the reason for the downward trend in the specific surface area (Fig. S3c–f†).

TEM images in Fig. 5a, e and i confirm the hollow character of the CeMnO$_x$ catalysts with uniform diameter and thickness, in consistent with the SEM images. From the TEM images of CeMnO$_x$-1 in Fig. 5b and c, we can see some large nanocrystals with high crystallinity on the surface. For CeMnO$_x$-3, large nanoparticles on the surface disappear and the structure of the sphere gets puffy (Fig. 5f and g). The thickness of the hollow sphere increases obviously from CeMnO$_x$-3 to CeMnO$_x$-5, and the structure becomes more compact (Fig. 5j). For the HRTEM images of the three catalysts, there is apparent lattice fringe with a spacing of about 0.31 nm, corresponding to the (111) plane of face-centered cubic CeO$_2$. No lattice fringe indexed to MnO$_x$ species can be observed, but there are some areas with amorphous structure (marked with red circles in Fig. 5c, g and k), which attributes to part of Mn species that have not entered the CeO$_2$ lattice. We can see that there are more amorphous MnO$_x$ particles that well dispersed on the surface of CeMnO$_x$-3 than those in CeMnO$_x$-1. But with a further increase of Mn content, CeMnO$_x$-5 is nearly covered by a layer of amorphous MnO$_x$.
particles, illustrating the high amount of Mn (Fig. 5k). The diffraction points and rings in SAED in Fig. 5d prove the coexistence of pure CeO2 and few CeMnOx with low crystallinity. For CeMnOx-3, the diffraction points that indexed to CeO2 was hard to be observed, further confirming the formation of a large amount of amorphous MnOx on the surface of CeMnOx solid solution (Fig. 5h). The diffraction points disappeared totally for CeMnOx-5, caused by the coverage of the MnOx layer on CeO2. The structural differences would affect the catalytic activity (Fig. 5l).

3.2 Chemical states of the catalysts

The chemical compositions of CeO2 and CeMnOx were investigated by XPS (Fig. 6). Ce 3d spectra (Fig. 6a) are fitted to eight peaks by deconvolution and labelled as U and V, contributing to 3d5/2 and 3d3/2 spin–orbit components of Ce, respectively.42,43 These peaks marked with V, V′, V″, U, U′ and U″ are attributed to the Ce4+ species while V′ and U′ are assigned to the Ce3+ species. The relative content of Ce3+ can be calculated by Ce3+/ (Ce3+ + Ce4+) based on the peak area and the results are shown in Table 2. The relative surface Ce3+ content increases slightly, reaches a maximum for CeMnOx-3. According to literatures, toluene catalytic oxidation on CeO2 and MnOx usually conforms to Mars–van-Krevelen (MvK) mechanism, in which oxygen atoms on the surface of the catalysts are key factors as they participate in the reaction.38 So, the concentrations of oxygen vacancies and surface adsorbed oxygen species on the catalysts should be investigated deeply. Generally, nonstoichiometric Ce3+ species in CeO2 leads to the generation of crystal defects and oxygen vacancies to maintain electrostatic balance following the reaction: 4Ce4+ + O2 → 4Ce4+ + 0.5O2 + 2e− (□) → 2Ce4+ + 2Ce3+ + 0.5O2 + □ (□ represents oxygen vacancy).38,44–47 Therefore, higher Ce3+ content indicates more oxygen vacancies, contributing to superior redox properties and excellent catalytic activity. The corresponding XPS spectra of Mn 2p for CeMnOx are deconvoluted into three main peaks with binding energies at 640.5, 641.7 and 643.0 eV (Fig. 6b), which are assigned to the spin–orbital of Mn2+, Mn3+ and Mn4+ species, respectively. The results in Table 2 show that CeMnOx-3 has the largest concentration of Mn with a lower valence state (52.5%). The existence of more Mn2+ and Mn3+ also imply the formation of more oxygen vacancies, similar to the effect of Ce3+.

All the O 1s spectra in Fig. 6c can be deconvoluted into three peaks located at about 529.6, 530.5, and 533.1 eV (Fig. 6c), attributing to the lattice oxygen (O1), adsorbed oxygen with low coordination (such as O2−, O2− and O−, denoted as O2), and carbonates (O3), respectively.40,48 The percentages of adsorbed oxygen for all the catalysts exhibit the same trend with Ce3+ and Mn2+ with
lower valence states, consistent with the conclusion that Ce and Mn species with lower valence states are benefit for increasing the amount of surface adsorbed oxygen.\textsuperscript{49} Strong interaction between Ce and Mn weakens the Ce–O bonds located at the interface of MnO\textsubscript{2} and CeO\textsubscript{2}, and increases the mobility of lattice oxygen. As a result, oxygen vacancies can be easily formed and surface adsorbed oxygen species are enhanced consequently, which are benefit for toluene oxidation according to the MvK mechanism.

### 3.3 Reducibility of the catalysts

Redox properties of the catalysts were investigated by H\textsubscript{2}-TPR and the curves were exhibited in Fig. 7. CeO\textsubscript{2} exhibits a reduction peak at about 520 °C, which can be ascribed to the consumption of H\textsubscript{2} by CeO\textsubscript{2}\textsuperscript{48} After the introduction of Mn, the reduction peaks of CeMnO\textsubscript{2}-1 and CeMnO\textsubscript{2}-2 shift to the lower temperature continually, implying that the introduction of Mn ions can improve the reduction reducibility of CeO\textsubscript{2} significantly. It should be noted that a broad band of H\textsubscript{2} consumption for CeMnO\textsubscript{2}-2 began to occur at about 300 °C, which can be assigned to the reduction of MnO\textsubscript{2} species.\textsuperscript{48} With the increase of Mn content, CeMnO\textsubscript{2}-3 exhibit three peaks at about 230, 285 and 354 °C, corresponding to the reduction of Mn\textsuperscript{4+} to Mn\textsuperscript{3+}, Mn\textsuperscript{3+} to Mn\textsuperscript{2+} and partial reduction of surface ceria, respectively.\textsuperscript{50–52} For CeMnO\textsubscript{2}-4 and CeMnO\textsubscript{2}-5, even the peaks shift to high temperature again, they are still much lower than that of pure CeO\textsubscript{2}. It is reported that –Mn–O–Ce– bond of CeMnO\textsubscript{2} hollow spheres can reduce the oxygen vacancy formation energy remarkably, and then strengthen the mobility of oxygen species from the bulk to the surface when compared with pure ceria.\textsuperscript{23} These results indicate that the addition of an appropriate amount of Mn into the CeO\textsubscript{2} lattice can lead to high mobility and XPS results. Combined with all these results above, it is reasonable to speculate that the CeMnO\textsubscript{2} can exhibit better promote the release of the lattice oxygen, inconsistent with the catalytic activity than pure CeO\textsubscript{2}, and CeMnO\textsubscript{2}-3 should be the best one.

### 3.4 Catalytic activity

The catalytic oxidation of toluene over the hollow structured CeMnO\textsubscript{2} catalyst is present in Fig. 8a. In general, the activities of all catalysts reveal a similar positive correlation with the reaction temperature. CeO\textsubscript{2} shows the lowest catalytic activity, whose \( T_{50} \) and \( T_{90} \) are as high as 310 and 369 °C, respectively. After the introduction of Mn, all the CeMnO\textsubscript{2} exhibit better performance than CeO\textsubscript{2}, with the following order: CeMnO\textsubscript{2}-3 > CeMnO\textsubscript{2}-4 > CeMnO\textsubscript{2}-5. This result demonstrates that the introduction of Mn can improve the catalytic activities due to the synergistic effect between Ce and Mn, especially for CeMnO\textsubscript{2}-3, the complete conversion temperature of toluene is only 280 °C, while the conversion is only 8.9% for CeO\textsubscript{2} at the same temperature.

It is reported that with excess oxygen, the catalytic oxidation of toluene follows first-order kinetics with the toluene concentration.\textsuperscript{14–16} When the toluene conversion is less than 20%, the ln \( r \) dependence of \( 1/T \) can be used to calculate apparent activation energies (Fig. 8b). For clarification, the reaction rates and activation energies calculated from the slope of the linear fit of the Arrhenius scatter plots were listed in Table 3. The reaction rate over CeMnO\textsubscript{2}-3 is 0.141 μmol g\textsuperscript{-1} s\textsuperscript{-1}, the highest among these catalysts. \( E_a \) for CeMnO\textsubscript{2}-3 is the lowest and increased with the order: CeMnO\textsubscript{2}-3 < CeMnO\textsubscript{2}-4 < CeMnO\textsubscript{2}-5 < CeMnO\textsubscript{2}-2 < CeMnO\textsubscript{2}-1 < CeO\textsubscript{2}. The highest reaction rate and lowest \( E_a \) value for CeMnO\textsubscript{2}-3 both confirm its excellent performance on toluene oxidation.

### 3.5 Structure–activity relationships

The activation ability of oxygen molecules for catalysts is an essential factor in evaluating their catalytic activity. It has been proved that the surface oxygen vacancies are favourable for the
adsorption and activation of $O_2$. Therefore, the catalysts with high oxygen vacancies may exhibit good catalytic performance. XPS spectra (Fig. 6) confirm that after the addition of Mn, the content of $Ce^{3+}$ species increase and give rise to more oxygen vacancies, favourable for the activation of $O_2$. Accordingly, O 1s spectra of CeMnO$_x$ confirm the existence of more surface-absorbed oxygens compared with CeO$_2$, which would increase the redox property of CeMnO$_x$ catalysts significantly. According to the MVK mechanism, O$_{av}$ (O$^{2-}$) on the surface of the catalyst are the active species. After being consumed of O$^{2-}$ in the oxidation, they can be regenerated by migration of electrophilic surface-absorbed oxygens (O$_2$$^{2-}$, O$^{2-}$ and O$^-$) into oxygen vacancies with the dissociation of O$_2$ in the feed continually (Scheme 2). Therefore, CeMnO$_x$ with the most $Ce^{3+}$ species and surface-absorbed oxygens showed the best catalytic activity. However, when Mn continues to increase, the surface MnO$_x$ species would increase while the Ce$^{3+}$ content decreases gradually (Table 2). From Fig. 5k, there was even a layer of amorphous MnO$_x$ that covered the solid solution CeMnO$_x$, inhibiting the contact between $-$Mn–O–Ce– and O$_2$. Therefore, the surface-absorbed oxygens and catalytic activity decreased correspondingly.

3.6 The stability test and water resistance

The stability of the catalysts is also a critical factor for practical application. Fresh CeMnO$_x$-3 was tested for the toluene conversion (inlet concentration 1000 ppm) as a function of time on stream at 280 °C. As shown in Fig. 9a, the catalyst was relatively stable for 10 h, with 100% toluene conversion. In the next 10 h, the conversion only exhibits a slight decrease, and is stable at 99%. After reacting for 20 h, the reaction system was cooled to room temperature and reheated to 200 °C for reusability test. It can be seen that in the second cycle, there is no apparent change in toluene conversion. Even after the third test, the toluene conversion can maintain 97.7%. Obviously, the catalyst has excellent catalytic stability and reusability for the oxidation of toluene, endowing it the possibility of future industrialization.

In practical application, moisture tolerance of the catalyst is another important factor to be considered as VOCs gas in the industry often contains water. Therefore, the influence of vapor on the long-term catalytic activity of CeMnO$_x$-3 under the feed gas stream including 5 vol% of water at 280 °C was investigated and the result was given in Fig. 9b. In the absence of water vapor, the toluene conversion maintained 100%, consistent with the results in Fig. 9a. After introducing water vapor into the reaction stream, the toluene conversion decreased to 95% directly and remained stable afterward. Once the water vapor was stopped, the conversion recovered to 97%. For the subsequent two cycles, the catalytic activity showed a similar trend and the toluene conversion was above 90% throughout the test. Finally, the toluene conversion could recover to 97% after the water vapor was out. Therefore, the catalyst owned excellent water vapor tolerance, which is a favorable factor for achieving industrial application.

4 Conclusions

In this work, we combined the template method and interfacial reaction to prepare a series of CeMnO$_x$ binary oxide hollow spheres with uniform morphology, diameter and thickness. Mn was incorporated by an interfacial redox reaction between KMnO$_4$ and Ce elements with low valence on the surface of SiO$_2$@CeO$_2$. The as-prepared binary oxides exhibit better catalytic activities than CeO$_2$ hollow spheres. CeMnO$_x$-3 exhibits the lowest $T_{1/2}$ (nearly 100 °C lower than that of CeO$_2$), excellent stability and H$_2$O resistance even with WHSV of 120 000 h$^{-1}$. Redox properties and surface oxygen vacancies of the binary oxide catalysts are improved as the addition of Mn would cause strong interaction between Ce and Mn, increasing of surface-absorbed oxygen species, which are critical to the enhanced catalytic performance.

Table 3 $r$ and $E_a$ for toluene combustion over CeO$_2$ and CeMnO$_x$ catalysts

| Catalysts | $r$ ($\mu$mol g$^{-1}$ s$^{-1}$) | $E_a$ [kJ mol$^{-1}$] |
|-----------|-------------------------------|----------------------|
| CeO$_2$   | 0.025                         | 84                   |
| CeMnO$_x$-1 | 0.055                         | 79                   |
| CeMnO$_x$-2 | 0.087                         | 66                   |
| CeMnO$_x$-3 | 0.141                         | 51                   |
| CeMnO$_x$-4 | 0.097                         | 59                   |
| CeMnO$_x$-5 | 0.070                         | 71                   |

* The values of $r$ for CeO$_2$ and CeMnO$_x$-1 were obtained at 250 °C and the others were obtained at 200 °C.

Scheme 2 Schematic illustration for the synergy effect of Ce and Mn in the CeMnO$_x$ catalyst.
Author contributions
Yuhua Zheng: methodology, analysis, writing and editing. Jing Zhou: synthesis. Xi Zeng and Dandan Hu, investigation and characterization. Fang Wang: data curation. Yanbin Cui: supervision, funding acquisition and review.

Conflicts of interest
There are no conflicts to declare.

Acknowledgements
This work is financially supported by the financial support from National Natural Science Foundation of China (No. 22076189) and the Open Research Fund Program of Key Laboratory of Cleaner Production and Integrated Resource Utilization of China National Light Industry (No. CP2021YB06).

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