Low Temperature Catalytic Performance of Manganese and Cerium Complex Oxide Catalyst towards Toluene

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Abstract: A series of MnOₓ(X)–CeO₂ complex oxide catalysts with various Mn/Ce mole ratios were prepared successfully by sol-gel method and were characterized by BET, XRD, SEM, H₂-TPR and XPS techniques, and the catalytic activity towards toluene were tested. The results showed that MnOₓ(X)–CeO₂ complex oxide catalysts presented superior low temperature catalytic activity than pure CeO₂ and MnOₓ. MnOₓ(0.6)–CeO₂ exhibited the highest catalytic activity with T₅₀=125℃ and T₉₀=197℃ under the condition of GHSV of 10000h⁻¹ and toluene concentration of 100ppm. The characterization results also indicated that the catalytic activity was relevant closely with specific surface area, catalyst morphology and valence of manganese oxides. Also, MnOₓ(X)–CeO₂ formed solid solution with fluorite structure after the introduction of manganese, and produced quantities of manganese species, atom adsorbed oxygen and crystal oxygen, which promoted the adsorption and activation of gaseous oxygen and the mobility and transfer of active oxygen.

1. Introduction
Currently, Volatile Organic Compounds (VOCs) have become the main atmospheric pollutants, and catalysis is one of the most efficient methods to degrade VOCs [1]. As the widely use in the industry, the noble metal catalysts have the deficiencies including the shortage, valuableness and instability, though they have the advantage of high activity [2]. However, because of the high thermostability, inexpensive, and high catalytic activity, the oxide catalysts of transition metal have obtained abundant attentions. Relative to the single component transition metal oxide catalyst, the two or more components of the transition metal composite oxide might express higher catalytic activity and stability. Under certain conditions, the complex oxide catalysts might put up the same activity as the noble metal catalysts [3]. Using the Cu-Mn-Ce-Zr composite oxide as the catalytic combustion towards toluene, the reaction temperature can be lower than 200 ℃ [4]. With the reason of low-temperature activity and excellent oxygen storage capacity, the Mn-Ce- compound catalysts also gain amount of attractions. Yuan et al [5] have discovered that Ce-doped MnOₓ-CeO₂/TiO₂ has lower catalytic temperature than the MnOₓ/TiO₂, with the removal rate higher than 90% in the range of 300-
400°C. Liu et al [6] have expressed that the Ce/Mn compounds have higher oxidation state than the MnOx by the activation of MnOx’s lattice oxygen, which might show up a more superior catalytic activity towards formaldehyde. As is known to all, series of factors might increase the low-temperature activity. However, the method to efficiently increase the activity and the way to control the differences of catalyst surface and the composition of species are still unclear. Herein, we apply the sol-gel method to investigate a series of MnOx(X)–CeO2, exploring the effect of the Mn-/Ce- doped catalysts with different molar ratio towards toluene, characterized by BET, XRD, H2-TPR and XPS techniques, and the catalytic activity towards toluene were tested.

2. Materials and Methods

2.1. Catalysts
The sol-gel method was used to investigate a series of MnOx(X)–CeO2 catalysts. In typically, adding a certain amount of Cerium nitrate (Ce(NO3)3·6H2O) and Manganese acetate (Mn(CH3COO)2·4H2O) to the ethanol, then adding some Citric acid to form a homogeneous solution, with stirring and heating in water bath at 80°C. After reaction, drying for 12h and then roasting at 550°C for 5h, different composition of MnOx–CeO2 catalysts were obtained. Additionally, the pure MnO2 catalyst and CeO2 catalyst were prepared using the same method.

2.2. Catalyst Characterization
XRD measurements were taken on a D8 Advance diffractometer with Ni-filtered Cu Kα radiation (k = 0.15418 nm, 40 kV, 40 mA) in the 2θ range of 5-90°. The XRD phases were identified by comparison with the reference data from Joint Committee on Powder Diffraction Standards (JCPDS) data files. The specific surface area, pore volume and pore size of the samples were determined by nitrogen adsorption on an ASAP 2020 M, and the BET method was utilized to calculate the specific surface area (S BET). H2-TPR experiments were performed with an Auto Chem II. The samples were pretreated in Ar at 300°C for 30min. After that, the experiments were carried out from 50°C to 900°C at a heating rate of 10°C/min in 10% H2/Ar (30 mL/min). The H2 consumption was determined by a TCD detector. XPS was used to analyze the chemical state and surface composition of samples. The binding energy calibration was performed using the Cls peak in the background as the reference energy (284.6 eV). The peak-differentiation-imitating was obtained through the XPS Peak 4 program.

2.3. Catalyst activity test
The catalyst test apparatus are composed of the valve system, the reactor and the detector, with using the toluene as target reactant. An air stream bubbling through a saturator filled with liquid toluene carried toluene vapor. The toluene destruction efficiency as a function of reaction temperature was measured in the case of space velocities of 10,000 h⁻¹. All gases were controlled by mass flow meters. Reactants and products were analyzed by gas chromatograph (GC-7890II) with FID detector.

3. Results and Discussion

3.1 Catalyst activity evaluation
The catalytic activities of the as-prepared catalysts towards toluene are shown in Fig.1. The catalyst of single oxide has only low activity towards toluene, the 50% conversion temperature (T50) of CeO2 and MnOx are 185°C and 155°C, with the 99% conversion temperature (T99) are over 300°C and 225°C, respectively. Compared with the single oxide, the manganese and cerium complex oxide catalysts have more excellent low-temperature activity, with the toluene conversion rate is above 90% when the temperature more than 200°C. As shown in Fig.1, the MnOx(0.6)-CeO2 might have the best activity, the T50 and T99 are 125°C and 197°C. The catalytic activity orders of MnOx(X)-CeO2 are from MnOx(0.6)-CeO2, MnOx(0.4)-CeO2, MnOx(0.8)-CeO2, MnOx(0.2)-CeO2, MnOx to CeO2 in sequence.
The above results might be attributed to the high oxygen storage capacity of CeO$_2$, increasing the dispersity of Mn. What’s more, CeO$_2$ and MnOx exist the synergistic effect, which might enhance the catalytic activity towards toluene.

3.2 BET analysis
The specific surface area of the MnOx(X)-CeO$_2$ are listed in Table.1. The results express that the specific surface area of MnOx and CeO$_2$ are 11.96m$^2$/g and 15.12m$^2$/g respectively, indicating that both the two single oxide have relatively low specific surface area. Compared with the above two samples, the CeO$_2$ doped manganites (MnOx(X)-CeO$_2$) get much larger specific surface area, which can be attributed to the lattice imperfection ,and the lattice imperfection causing by the replacement of Mn$^{n+}$ can make the crystalline and the average crystallite size decrease, leading the specific surface area enlarge[7,8]. With the combination of the above 3.1, we can obviously find that moderate Ce-doped and the large specific surface area can develop the catalytic activity towards toluene, revealing that the Ce-doped and the specific surface area are the important factors to the catalytic performance.

| MnOx(X)-CeO$_2$ | CeO$_2$ | MnOx(0.2)-CeO$_2$ | MnOx(0.4)-CeO$_2$ | MnOx(0.6)-CeO$_2$ | MnOx(0.8)-CeO$_2$ | MnO$_x$ |
|-----------------|--------|------------------|------------------|------------------|------------------|--------|
| Surface area (m$^2$/g) | 15.12  | 54.87            | 75.27            | 67.44            | 73.40            | 11.96  |

3.3 XRD
Fig.2 appears the x-ray diffraction patterns of MnOx(X)-CeO$_2$ catalysts. As shown in Fig.2, the peaks of the obtained spectrograms are fitting with the characteristic peaks of cubic fluorite structure CeO$_2$ [9]. Meanwhile, the spectrograms of MnOx appear the characteristic peaks of Mn$_2$O$_3$ at 23.1°, 33.9° and 55.2°, with appearing the characteristic peaks of MnO$_2$ at 45.1° and 65.6°, but there is only one characteristic peak of Mn$_3$O$_4$ at 38.1°[10],which suggest that most existence form of the MnOx catalysts are present in high-valent manganese oxides through the sol-gel method. Studies [11] have shown that the activity order of the non-load type manganese oxide was Mn$_3$O$_4$ > MnO$_3$ > MnO, suggested that numerous of Mn$_3$O$_4$ and MnO$_2$ was benefit to the enhancement of the low-temperature activity.

The XRD patterns of MnOx(0.2)-CeO$_2$ to MnOx (0.8)-CeO$_2$ show only the characteristic diffraction peaks of CeO$_2$ cubic fluorite structure, and there is no characteristic peak of MnO$_x$. It is presumably in the reason of CeO$_2$ and MnOx forming a fluor spar structure of the Mn-Ce solid solution or the amorphous manganese oxide. In addition, it can be seen from Fig.2 that the main diffraction...
peak of MnO\(X\)-CeO\(_2\) catalyst is similar to CeO\(_2\) with the increase of Mn introduction, indicating that the doping of Mn does not change the main structure of CeO\(_2\), but the diffraction peaks of the composite oxide are broadened and passivated, and the position of the CeO\(_2\) characteristic diffraction peaks is shifted in the high angle direction, indicating that more manganese species enter into the CeO\(_2\) lattice and form a manganese-cerium solid solution, causing the CeO\(_2\) cell shrinkage[12]. This is because smaller manganese ions inset into the CeO\(_2\) lattice instead of the cerium ion, resulting in smaller interplanar spacing and unit cell parameters [13]. Therefore, the addition of Mn is beneficial to the formation of manganese solid solution.

![XRD patterns of the MnO\(X\)-CeO\(_2\) complex oxide catalysts](image)

**Figure 2.** XRD patterns of the MnO\(X\)-CeO\(_2\) complex oxide catalysts

### 3.4 H\(_2\)-TPR

Fig.3 expresses the H\(_2\)-TPR graph of the MnO\(X\)-CeO\(_2\). From the Fig.3, there are two big reduction peaks, and the relative temperatures of reduction peaks are 338 ℃ and 446 ℃. According to the literatures [14], the reduction peak of lower temperature means MnO\(_2\) and Mn\(_2\)O\(_3\) are reduced to Mn\(_3\)O\(_4\), the other peak means Mn\(_3\)O\(_4\) are reduced to MnO, which means MnO\(X\) finally changed into MnO. Pure CeO\(_2\) shows two weak reduction peaks at about 380 ℃ and about 500 ℃, which are relative with the reduction of Ce\(^{4+}\)[15]. It can be seen from the peak area that CeO\(_2\) consumes less H\(_2\) than MnO\(X\). Compared with the reducibility of MnO\(_X\), the MnO\(X\)-CeO\(_2\) also appears two peaks of reduction, and reduction temperature is shifted to the low temperature, indicating that the Mn-doped

![H\(_2\)-TPR profiles of MnO\(X\)-CeO\(_2\) catalysts](image)

**Figure 3.** H\(_2\)-TPR profiles of MnO\(X\)-CeO\(_2\) catalysts
can improve the redox performance of the catalyst. Based on XRD results (3.3), importing moderate amount of Mn into the MnO<sub>X</sub>(X)-CeO<sub>2</sub> can generate more lattice defects and oxygen vacancies developing the ability of oxygen migration, transformation and release capacity, with enhancing the redox capacity of the catalyst. However, with excessive amount of Mn introduction, some Mn ions accumulated on the catalyst surface rather than entering into the solid solution structure, which might weaken the flow of oxygen performance.

3.5 XPS

Fig. 4 expresses the XPS graph of the O1s peak fitting, and the results are shown in Table 2. As seen in Fig.4, pure CeO<sub>2</sub> appears three different binding energy O1s peaks, the binding energies appearing in 533eV, 531eV and 528eV are assigned to O<sup>-2</sup>, O<sup>-</sup> and O<sup>-</sup>, respectively[16]. The O1s peak of lattice oxygen (O<sup>-2</sup>) appears to migrate toward high energy with being attributed to the process of “O→Mn” electronic transmission [17]. In addition, compared with pure CeO<sub>2</sub>, MnO<sub>X</sub>(X)-CeO<sub>2</sub> have stronger ability of oxygen adsorption. The results show that the adsorbed oxygen atom (O<sup>-</sup>) is a reactive oxygen species of catalytic combustion activity [18]. From the Table.2, MnO<sub>X</sub>(0.6)-CeO<sub>2</sub> has gotten more lattice oxygen leading the strength of the catalytic activity at low temperature, and the result is consistent with the results of H<sub>2</sub>-TPR (3.4).

![Figure 4. O1s XPS spectra of the MnO<sub>X</sub>(X)-CeO<sub>2</sub> catalysts](image)

| Catalysts       | Mn distribution (%) | Oxygen distribution (%) |
|-----------------|---------------------|-------------------------|
|                 | Mn<sup>4+</sup>     | Mn<sup>3+</sup>/ Mn<sup>2+</sup> | O<sup>-2</sup> | O<sup>-</sup> | O<sup>-</sup> |
| CeO<sub>2</sub> | --                  | --                      | 60.1          | 28.9          | 11           |
| MnO<sub>X</sub>(0.6)-CeO<sub>2</sub> | 75.6                | 24.4                    | 60.9          | 32.0          | 7.1          |
| MnO<sub>X</sub> | 56.8                | 43.2                    | 68.2          | 23.3          | 8.5          |

Additionally, Fig.5 expresses the XPS graph of the Mn2p peak fitting. As shown in Fig.5, pure MnO<sub>X</sub> appears three different binding energy Mn2p peaks, the binding energies appearing in 641-643eV and 640eV are assigned to Mn<sup>4+</sup>and Mn<sup>3+</sup>/ Mn<sup>2+</sup>, respectively. Compared with pure MnO<sub>X</sub>, MnO<sub>X</sub>(0.6)-CeO<sub>2</sub> catalyst has more Mn<sup>4+</sup>,and the range of energy level become wider, meaning that high-valence manganese species are more conducive to improve the catalytic reaction of low temperature activity, and the result is consistent with the results of XRD(3.3).
3.6 Morphology of MnOx(0.6)-CeO2
The morphologies of the as-synthesized samples were examined by SEM. As observed in Fig. 6A and Fig.6B, the pictures express the MnOx and CeO2 are mainly composed of nanorods, combined with the results of XRD (Fig.2). What’s interesting, from the Fig.6C, the morphology of MnOx(0.6)-CeO2 was a structure of nano-cluster, because of the surface energy reduction. In order to develop the Ce-doped formation, the high-resolution image of MnOx(0.6)-CeO2 (Fig.6D) show that the nano-blocks of Cerium oxide equably distributed on the MnOx, providing a large number of catalytic active sites. In addition, the Mn-Ce solid solution can be further improved the co-catalyst of CeO2, leading an excellent catalytic activity to low temperature catalytic combustion towards toluene [15].

3.7 Stability test of MnOx(0.6)-CeO2
In commercial applications, catalytic stability as well as activity, is a very important factor. The stability performance of the MnOx (0.6)-CeO2 catalyst is tested under the condition of GHSV of 10000h⁻¹ and toluene concentration of 100ppm is shown in Fig.7. We can easily find from the figure that the toluene conversion still approach to 90% after 50 hours reaction period at 197°C. It means that
the as-prepared catalyst has an excellent stability in the catalytic combustion towards toluene.

![Toluene Conversion %](image-url)

**Figure 7. Stability test of MnOx(0.6)-CeO₂ catalyst**

### 4. Conclusions

Among the MnOₓ(X)-CeO₂ catalysts prepared, the MnOx(0.6)-CeO₂ exhibits the highest catalytic activity with Tₙ₀=125°C and T₉₀=197°C under the condition of GHSV of 10000 h⁻¹ and toluene concentration of 100ppm. The low-temperature catalytic activity of MnOₓ(X)-CeO₂ towards toluene is assuredly relative to the specific surface area, manganese oxide morphology and manganese oxide valence state. The interaction between MnOₓ and CeO₂ form the fluorite structure solid solution, a large number of high valence manganese species, O⁻ and O²⁻, promoting the gaseous oxygen adsorption on the catalyst surface, migration, activation and conversion of reactive oxygen species. Additionally, the MnOx(0.6)-CeO₂ catalyst has an excellent stability.

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