ONE-STEP SYNTHESIS OF BINARY MN–CE OXIDES BY A REDOX-PRECIPITATION AS HIGHLY EFFICIENT THERMAL CATALYSTS FOR THE RESIDUAL METHANE OXIDIZING

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Abstract. A series of Mn-Ce catalysts with different ratio of Mn-to-Ce were prepared by a redox-precipitation method, and their catalytic performance in lean methane combustion was investigated. A plethora of structural (XRD), textural (BET, FSEM), and spectroscopic (XPS) methods have been applied for characterization. The results show that the catalytic performance of the investigated samples is strongly related to the ratios of Mn-to-Ce. Mn-Ce catalyst with an atomic Mn/Ce ratio of 9/1 provided with a larger specific surface area, pore volumes, abundant manganese species of higher valence (Mn$^{4+}$), Cerium species of lower valence (Ce$^{3+}$), and lattice oxygen.

1. Introduction

Methane was classified as one of pollution, due to the warming potential of methane is over 20 times that of CO$_2$ (100 years)[1]. Mine Gas, about 8% of total methane emissions, is one of the most important methane emission [2]. Catalytic combustion is a promising way to remove trace amounts of methane (0.1-1%) in VAM, due to lower cost and safety, compared with other methods [2]. And the key to this technology is the catalyst’s development of ignition at low temperature and stable at high temperature [3].

Noble and non-noble metal catalysts are the main kinds of catalysts. Noble metal-based catalysts exhibit higher efficiency in low-temperature windows, however, the higher price has turned scientist’s attention toward inexpensive and thermally stable materials, such as Metal Oxide Catalyst. Metal Oxide catalysts could be more suitable materials, comparing with the noble-metal-containing catalysts.

Zhang et al.[4] reported that Ni-Mn-O solid solution is beneficial for lean methane catalytic combustion at low temperature, due to abundant highly dispersed higher oxidation state of manganese (Mn$^{4+}$). Hu et al.[5] reported that the presence of ceria has a strong influence on the crystal structure, surface phase composition and reducibility of catalyst, which is beneficial for catalytic performance.

The above results present excellent redox ability of Mn and Ce metal. The Mn-Ce catalyst has been investigated extensively in terms of NH$_3$-SCR[6], CWAO[7], etc, especially in low temperature. However, there are only a few reports about lean methane catalytic combustion by Mn-Ce catalyst [1,8–11], due to the particle size, the surface texture of catalyst has the effect on the performance of the catalyst.

Many methods for preparing Mn-Ce catalysts, such as co-precipitation, sol-gel, and hydrothermal methods, have been reported [12]. Co-precipitation has been applied extensively in the industry...
compared with other methods, due to features of the simple process and low cost. However, uneven pH value results in agglomeration. The redox-precipitation is an improved method of co-precipitation, which could reduce the influence of swing pH value, improve the distribution of Mn-Ce oxides and produce $\alpha$-MnO$_2$[6]. The performance of $\alpha$-MnO$_2$ is better than that of other manganese oxides[13].

In this paper, a series of Mn-Ce catalysts with different ratio of Mn-to-Ce were prepared by a redox-precipitation, and their catalytic performance in lean methane combustion was investigated. The physicochemical properties of the catalyst were characterized, furtherly. The ratio optimization of the catalyst was performed, which is an important parameter of the methane combustion process.

2. Experimental procedure

2.1. Catalyst Synthesis

A series of Mn-Ce catalysts with different ratio of Mn-to-Ce were prepared by a redox-precipitation, following the similar procedures as described elsewhere[14,15]. Briefly, consisting in the titration at constant pH value (4.5±0.3, by addition of 0.4M KOH) of the Mn(NO$_3$)$_2$ (AR 50wt.% in H$_2$O) nitrates precursor with a solution of (NH$_4$)$_2$Ce(NO$_3$)$_6$ (AR 99.0%) and KMnO$_4$ (GR). After titration, the precipitation was washed by Ultra-pure water and ethanol three times, after that, the solid was dried at 100°C (12 h) and further calcined (6 h) in the air at 500°C. According to the Mn molar content in the catalyst (30%, 50%, 70%, 90%, 100%), the catalyst prepared in this way is denoted as Mnx (x=30, 50, 70, 90, 100).

2.2. Characterization

The specific surface area and pore volume of the catalysts were calculated, using the Brunauer-Emmet-Teller (BET) and Barrett-Joyner-Halend (BJH) equation based on data obtained by an N$_2$ adsorption-desorption experiment on a physical adsorption station (ASAP2020, Micromeritics). The XRD pattern was recorded on X’pert$^3$ Powder X-ray diffractometer (PANalytical, Inc.) operated at 60 kV and 60 mA with a scan angle of 5°-85°. A Nova NanoSEM 450 microscope was also used for image observation of the samples at the accelerating voltage of 10 kV. The XPS spectra were conducted with XPS equipment (AXIS-ULTRADLD-600W Kratos). Transmittance spectra were recorded using a UV-Vis spectrophotometer (Shimadzu SolidSpec-3700) at room temperature.

2.3. Catalytic performance measurements

The performance of a series of catalysts in the oxidation of methane was measured in a fixed-bed reactor (id=6mm), as shown in Figure 1. The reaction gases typically consisted of 1% CH$_4$, 10% O$_2$ and the balance N$_2$ to simulate the flue gas. The concentrations of CH$_4$, CO, and CO$_2$ at reactor inlet and outlet were measured by GC9700II (FULI Instruments) with two detectors of FID and TCD ( no CO and H$_2$ were detected during the experiments, and methane was totally oxidized to CO$_2$). The
reaction gas concentrations were accessed to the reactor after 30 mins later of the temperature of the tube furnace becoming the elevated value, in order to make sure the accuracy of the measurement. Conversions of CH4 was calculated as follows:

\[ X_{CH_4} = \frac{C_{in} - C_{out}}{C_{in}} \times 100\% \]

Where \( C_{in} \) and \( C_{out} \) are the CH4 concentration in the feed gas and products (vol%), respectively;

3. Results and discussion

3.1. Catalytic performance
The performance of Mnx is presented in Fig. 2. The results indicated the performance of catalysts were excellence over 560°C, and all conversion is over than 90%. Mostly, the temperature to reach a methane conversion of 50% (T50) is regarded as a criterion of the catalytic performance for methane combustion, especially for MnOx [1]. The Mn90 catalyst showed optimal performance, and 50% of methane conversion occurs at ~446°C. The performance of catalysts is improved with the content of Mn increasing from 30 to 90%, while the performance decreases with the Mn content increasing furtherly.

Compared with Mn90 catalyst, the Mn100 catalyst exhibited the same conversion efficiency at ~456 °C, 10°C higher than the Mn90 catalyst, indicating that Mn90 had higher catalytic activity.

3.2. BET results
The specific surface areas and pore volumes of Mn-Ce catalysts are listed in Table 1. The specific surface of catalysts tended to increase first and then decrease, indicating giving an optimum parameter of specific surface areas and pore volumes with an optimal Mn content. And the specific surface areas and pore volumes of Mn90 were larger than those of Mn100, which is consistent with the literature [15]. The specific surface areas and pore volumes of Mn50, Mn70, and Mn90 are larger than those of Mn30 and Mn100 catalysts. There are more active sites over the catalyst, larger specific surface areas, and pore volumes, beneficial for the performance of catalyst improving.

| Sample | BET Surface Area(m²/g) | Pore Volume(*10⁻²cm³/g) | Average Pore(nm) |
|--------|------------------------|--------------------------|------------------|
| Mn30   | 100                    | 39.16                    | 10.7177          |
| Mn50   | 118                    | 78.59                    | 21.6493          |
| Mn70   | 117                    | 76.29                    | 23.6467          |
| Mn90   | 111                    | 62.38                    | 21.8270          |
| Mn100  | 39                     | 25.30                    | 25.7554          |

3.3. XRD results
The XRD patterns of Mnx catalysts are shown in Fig. 3. It is clearly observed that the crystal peaks of CeO₂ (JCPDS 34-0394), Mn₅O₈ (JCPDS 39-1218) and MnO₂ (JCPDS 24-0735) when the ratio of Mn-to-Ce is lower than 7/3. There are lower intensity and broader half-peak width of peaks, with the ratio increasing from 3/7 to 7/3, which indicates stronger interaction of Mn and Ce [8]. However, the new crystal peaks of KMn₈O₁₆ (JCPDS 29-1020) showed the characteristic peaks (12.75 and 18.06, especially) and the peaks of MnO₂ disappear. There is no report about KMn₈O₁₆ in Mn-Ce catalyst for lean methane combustion[1,8–11], and just one report about the Mn-Ce catalyst made by a redox-precipitation for benzyl alcohol oxidation[16]. According to the literature, the performance of methane catalytic combustion decrease in the order of KMn₈O₁₆ ≈ MnO₂ > Mn₅O₈, which is consistent with our experience result.

Compared with Mn100, the intensity of Mn90 catalyst’s peaks is lower and broader, which indicated MnOx noncrystalline or Mn-Ce solid-solution catalyst. This means that the catalyst with a
given number Cerium can improve the electron transfer between different Mn ion, and enhance the performance of the catalyst[6].

3.4. SEM and EDS results

SEM images of Mnx catalysts are shown in figure 3. The texture and morphology of Mnx catalysts are markedly different. There are serious sintering and agglomeration when the ratio of Mn-to-Ce are 3/7 and 5/5. The size of catalyst particles would be smaller with Mn content increasing. There are many nanorods and nanosphere, when the ratio is 9/1 or 10/0, especially. As is known, the performance of the catalyst is better with smaller average particle size, consistent with the literature [6].

To evaluate the effect of different ratio on the dispersion of Mn and Ce on the catalyst surface, the surface Mn/Ce atomic ratios were calculated based on the EDS data, showed in figure 3. The ratio of Mn-to-Ce on the catalyst surface is lower than the theoretical value when the ratio of Mn-to-Ce is no more than 7/3. The Mn element on the surface is lower than the theoretical value, due to the interaction of different elements. The all ionic radii of Mn$^{2+}$(0.083nm), Mn$^{3+}$(0.066nm) and Mn$^{4+}$(0.056nm) are smaller than that of Ce$^{3+}$(0.103nm) and Ce$^{4+}$(0.099nm), due to partial Mn cations doping into Ce lattice, forming Mn-Ce solid solution[1]. However, when the ratio of Mn-to-Ce is 9/1, the ratio of Mn-to-Ce is higher than the theoretical value, which may be due to the KMn$_8$O$_{16}$ crystal. The incorporation of Ce cations dopes into the KMn$_8$O$_{16}$ lattice in Mn90 sample, due to that the MnO$_6$ octahedra has a 2 $\times$ 2 tunnel structure with the size of 0.46 $\times$ 0.46nm[16] and the tunnel radius of MnO$_6$ octahedra is bigger than ionic radii of Ce$^{3+}$ and Ce$^{4+}$.

3.5. XPS Analysis

| Sample | Mn$_{2p3/2}$ position(eV) | Mn$^{4+}$ | Mn$^{3+}$ | Ce$^{3+}+Ce^{4+}$ | O1s position(eV) | O$_{\alpha}$ | O$_{\beta}$ | O$_{\omega}$ | O$_{\alpha} + O_{\beta}$ |
|--------|-------------------------|----------|----------|-----------------|------------------|-----------|----------|-----------|------------------|
| Mn30   | 642.9                   | 641.9    | 0.72     | 0.11            | 529.5            | 531.4     | 533.0    | 0.64      |
| Mn50   | 642.5                   | 641.6    | 0.94     | 0.17            | 529.4            | 531.4     | 533.0    | 0.70      |
| Mn70   | 642.4                   | 641.6    | 1.95     | 0.19            | 529.5            | 531.4     | 533.0    | 0.83      |
| Mn90   | 642.6                   | 641.6    | 3.56     | 0.28            | 529.7            | 531.6     | 533.0    | 0.85      |
| Mn100  | 642.6                   | 641.6    | 7.67     | -               | 529.7            | 531.6     | 533.0    | 0.79      |

XPS spectra of Mnx was shown in Figure 4 and detail data were listed in Table 2. Figure 4(a) shows the Mn2p XPS spectra of Mnx catalysts. Based on the literature and previous XRD analysis, the
value state of Mn in the catalyst made by the redox-precipitation method is between 3+ and 4+, one mixed valence[13]. Mostly, the peaks approximately 642.4-642.9 eV and 641.6-641.9 eV[13] are attributed to the presence of Mn$^{4+}$ and Mn$^{3+}$ species, respectively (the Mn$^{2+}$ peak was ignored). It’s clear that the Mn$^{4+}$ content in catalyst increases gradually with Mn content increasing, which is consistent with the XRD results. The ratio of Mn$^{4+}$-to-Mn$^{3+}$ in Mn100 is about 7.67, which is similar to that in KMn$_8$O$_{16}$, indicating the existence of KMn$_8$O$_{16}$. The combustion rate of lean methane catalytic combustion is positively related to the ratio of Mn$^{4+}$-to-Mn$^{3+}$ in Mn-Ce catalyst[17].

Figure 4(b) shows the Ce3d XPS spectra of Mnx catalysts. The peaks named as u$$`, v$$`, u, v$$`, v$$` and v arise from the Ce$^{4+}$ contribution, while Ce$^{3+}$ is characterized by two other peaks [12]. The proportion of Ce$^{3+}$ in the catalyst increase from 0.11 to 0.28, when the ratio of Mn-to-Ce increases from 3/7 to 9/1, consistent with the changing trend of the catalyst performance. The oxygen vacancy and the active undersaturated bond would increase with the increase in the concentration of Ce$^{3+}$, promoting the oxygen adsorption and transfer processes, and improving the redox-ability of the catalyst [18].

Figure 4. The XPS spectra of Mnx catalysts: (1) Mn30; (2) Mn50; (3) Mn70; (4) Mn90; (5) Mn100

Figure 4(c) shows the O1s XPS spectra of Mnx catalysts. There is a double-peak structure at a range of 529.4-529.9 eV. O1s spectra were divided into three types peaks: the peak at BE of 529.6-529.9 eV was ascribed to the lattice oxygen (denoted as O$_{\alpha}$), the peak at BE of 531.4-531.6 eV was ascribed to chemisorbed oxygen (denoted as O$_{\beta}$), and the peak at a higher BE (above 533.0 eV) corresponded to adsorbed water (denoted as O$_{\omega}$)[6]. The process of organic compounds catalytic combustion occurs mostly via the Mars and van Krevelen mechanism [17], and the lattice oxygen of manganese oxide was considered to be the primary active species for activating the C-H bonds above 400°C, so the performance of catalyst increases, as the number of the lattice oxygen increases. The proportion of O$_{\alpha}$ in active oxygen tended to rise, then fall, with Mn content increasing, which is consistent with the change tendency of catalyst performance.

Thus, there are three parameters determining the performance of methane catalytic combustion: (1) higher value state of manganese species, (2) lower value state of Cerium species, and (3) higher content of lattice oxygen on the surface of the catalyst.

4. Results
The results obtained for Mnx catalysts, synthesized by a redox-precipitation, confirmed their performance for total combustion of CH$_4$ at low concentration (1 vol %). The results of this investigation lead us to draw the following conclusions:

- The performance of Mn90 catalyst is best (T50=~446°C) at 3000 ml/(h.g);
- The appropriate ratio of Mn-to-Ce is beneficial for the bigger specific surface areas and pore volumes.
- The appropriate ratio of Mn-to-Ce is beneficial for more KMn$_8$O$_{16}$, which improves the Mn content, oxygen vacancy, and lattice oxygen concentration.
- The appropriate ratio of Mn-to-Ce is beneficial for fine size for crystalline grain.

References
[1] Fiuk MM, Adamski A. Activity of MnOx–CeO2 catalysts in combustion of low concentrated methane. CATAL TODAY 2015;257:131–5.
[2] Setiawan A, Kennedy EM, Stockenhuber M. Development of Combustion Technology for Methane Emitted from Coal-Mine Ventilation Air Systems. ENERGY TECHNOL-GER 2017;5:521–38.

[3] Li X. Progress of development and utilization of coalbed methane in the world. Coal Process Compr Util 2006;41:1–5.

[4] Zhang Y G, Qin Z F, Wang G F, Zhu H Q, Dong M, Li S N, Wu Z W, Li Z K, Wu Z H, Zhang J, Hu T D, Fan W B, Wang J G. Catalytic performance of MnOx–NiO composite oxide in lean methane combustion at low temperature. APPL CATAL B-ENVIRON 2013;129:172–81.

[5] Hu Z, Qiu S, You Y, Guo Y, Guo Y, Wang L, Zhan W, Lu G. Hydrothermal synthesis of NiCeOx nanosheets and its application to the total oxidation of propane. APPL CATAL B-ENVIRON 2018;225:110–20.

[6] Sheng Z, Hu Y, Xue J, Wang X, Liao W. A novel co-precipitation method for preparation of Mn–Ce/TiO2 composites for NOx reduction with NH3 at low temperature. ENVIRON TECHNOLOG 2012;33:2421–8.

[7] Cybulski A. Catalytic Wet Air Oxidation: Are Monolithic Catalysts and Reactors Feasible? Ind Eng Chem Res 2007;46:4007–33.

[8] Li S, Song P, Zhang J, He X, Xie Y, Zhang Y, Wang R, Li Z, Zhu H. Morphological effect of CeO2-MnOx catalyst on their catalytic performance in lean methane combustion. J Fuel Chem Technol 2018;46:615–24.

[9] ChangChun L, Jun-Jie Y, Zheng J, YanXin T, ZhengPing H, XuWen H. Methane catalytic combustion on Ce (1-x) MnxO (2-a) mixed oxide catalysts. CHINESE J INORG CHEM 2007;02:217–24.

[10] Palmqvist AEC, Johansson EM, Järås SG, Muhammed M. Total oxidation of methane over doped nanophase cerium oxides. CATAL LETT 1998;56:69–75.

[11] Zhang H, Yang W, Li D, Wang X. Influence of preparation method on the performance of Mn–Ce–O catalysts. React Kinet Catal Lett 2009;97:263–8.

[12] Zhang P, Lu H, Zhou Y, Zhang L, Wu Z, Yang S, Shi H, Zhu Q, Chen Y, Dai S. Mesoporous MnCeOx solid solutions for low temperature and selective oxidation of hydrocarbons. NAT COMMUN 2015;6:8446.

[13] Wang X, Liu Y, Zhang Y, Zhang T, Chang H, Zhang Y, Jiang L. Structural requirements of manganese oxides for methane oxidation: XAS spectroscopy and transition-state studies. APPL CATAL B-ENVIRON 2018;229:52–62.

[14] Arena F, Trunfio G, Negro J, Fazio B, Spadaro L. Basic Evidence of the Molecular Dispersion of MnCeOx Catalysts Synthesized via a Novel “Redox-Precipitation” Route. Chem Mater 2007;19:2269–76.

[15] Arena F, Gumina B, Lombardo AF, Espro C, Patti A, Spadaro L, Spiccia L. Nanostructured MnOx catalysts in the liquid phase selective oxidation of benzyl alcohol with oxygen: Part I. Effects of Ce and Fe addition on structure and reactivity. APPL CATAL B-ENVIRON 2015;162:260–7.

[16] Dharmarathna S, King’ondu CK, Pedrick W, Pahalagadara L, Suib SL. Direct sonochemical synthesis of manganese octahedral molecular sieve (OMS-2) nanomaterials using cosolvent systems, their characterization, and catalytic applications. CHEM MATER 2012;24:705–712.

[17] Han Y, Chen L, Ramesh K, Widjaja E, Chilukoti S, Kesumawinata Surjami I, Chen J. Kinetic and spectroscopic study of methane combustion over α-Mn2O3 nanocrystal catalysts. J CATAL 2008;253:261–8.

Kumar M, Bhatt V, Kim J, Kim J-S, Kim B-S, Lee C-Y, Singh B, Yun J-H. Role of Ce3+ valence state and surface oxygen vacancies on enhanced electrochemical performance of single step solvothermally synthesized CeO2 nanoparticles. Electrochimica Acta 2018;284:709–20.