

Modified fly ash from municipal solid waste incineration as catalyst support for Mn-Ce composite oxides

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Abstract. Fly ash from municipal solid waste incineration was modified by hydrothermal treatment and used as catalyst support for Mn-Ce composite oxides. The prepared catalyst showed good activity for the selective catalytic reduction (SCR) of NO by NH₃. A NO conversion of 93% could be achieved at 300 °C under a GHSV of 32857 h⁻¹. With the help of characterizations including XRD, BET, SEM, TEM, XPS and TPR, it was found that hydrothermal treatment brought a large surface area and abundant mesoporous to the modified fly ash, and Mn-Ce composite oxides were highly dispersed on the surface of the support. These physical and chemical properties were the intrinsic reasons for the good SCR activity. This work transformed fly ash into high value-added products, providing a new approach to the resource utilization and pollution control of fly ash.

1. Introduction

Incineration is a mainstream solution for managing the increasing production of municipal solid waste (MSW) throughout the world. Although incineration reduces the volume of MSW, it generates second pollutants, such as flue gas, bottom ash and fly ash, that must subsequently be disposed of. Fly ash poses is classified as a toxic waste because it contains leachable heavy metals and highly toxic organic substances including dioxins, furans and PAHs, making fly ash management one of the most important environmental issues related to the MSW incineration.

Various technologies such as stabilization/solidification, thermal treatment and physical/chemical separation are now available for fly ash disposal or reuse. Fly ash is rich in some elements and compounds and therefore has some potential to be used as raw materials. In the view of recycling philosophy, the potential application of fly ash results in at least two advantages: first, the elimination of waste, and secondly, the use of a zero-cost raw material.^[1]

Hydrothermal method for processing fly ash with improved chemical stability was considered as a promising technology, which offers considerable advantages in terms of economic, technical and environmental performance^[1]. This method has been employed successfully for treating fly ash in alkali solutions (NaOH and KOH).^[2] The use of fly ash for the synthesis of zeolite compounds such as zeolites by the hydrothermal method in the NaOH solution has been demonstrated previously. Another hydrothermal processing strategy of MSWI fly ash is presented for obtaining tobermorite and katoite that are considered as stable minerals with low toxic potential.^[3]



The present study was undertaken to access the benefits of hydrothermal treatment of fly ash from MSW incineration to novel material for catalyst support. Mn-Ce composite oxides were loaded on this support material and their catalytic performances were investigated in the selective catalytic reduction (SCR) of NO by NH₃. In order to reveal the physical and chemical properties, the prepared catalysts were subjected to a range of analytical techniques, including X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), temperature programmed reduction (TPR), etc.

2. Experimental

2.1. Hydrothermal treatment

Fly ash that sampled from the waste incineration plant of Haikou, China was modified by hydrothermal treatment in 10 N NaOH solution in a Teflonlined autoclave at 130-150 °C for 24 h. The precipitate after hydrothermal reaction was washed with 0.1 N HCl solution for several times, then with distilled water till pH was close to 7 and filtrated afterwards. After dried at 80 °C overnight, the modified fly ash was obtained and denoted as MFA.

2.2. Catalyst preparation

The loading of Mn-Ce composite oxides (Mn/Ce molar ration at 5:1) on MFA was conducted by wet impregnation method. Manganese nitrate and cerium nitrate were dissolved in deionized water and then impregnated with the required amount of MFA. The mixture was stirred for 4 h, dried at 80 °C for 18 h and calcined at 450 °C for 3 h to give the final Mn-Ce composite oxides loaded catalysts that denoted as MnCe/MFA. Catalysts were grinded to 40-100 mesh before use. The as-prepared catalysts were denoted as *x*MnCe/MFA, where *x* referred to the weight ratio of the Mn-Ce composite oxides.

2.3. Characterization

A nitrogen adsorption apparatus (ASAP 2020, USA) was used to obtain the nitrogen adsorption-desorption isotherms and the physical information of catalysts. XRD analysis was performed by using X-ray diffraction with Cu K α radiation (model D/max RA, Rigaku Co., Japan). SEM (Phillips XL-30-ESEM) was used to observe the microstructures of the prepared catalysts. The structure and morphology of catalysts were examined by TEM (JEM-2010, Japan). The surface properties was investigated by XPS with Al K α X-ray radiation operated at 150 W. TPR experiments were carried out using a TP-5080 setup (Tianjin Xianquan Industry and Trade Development Co. Ltd, China). Samples of 50 mg was placed in the middle of quartz tube and fixed with silica wool. Prior to TPR experiment, samples were purified in pure N₂ at 350 °C for 1 h and then cooled to 70 °C. The TPR experiment was then carried out with the linear heating rate 10 °C /min from 70 °C to 800 °C in 4 % H₂/N₂.

2.4. SCR activity evaluation

SCR tests were performed in a fixed-bed reactor with 0.5 g catalysts under steady state. The gas composition were: 700 ppm NO, 700 ppm NH₃, 3% O₂ and balanced N₂. NO, SO₂, NO₂ and O₂ concentrations were monitored by a flue gas analyzer (ECOM D, rbr Messtechnik GmbH).

NO conversion is calculated as:

$$\text{NO conversion \%} = ([\text{NOx}]_{\text{in}} - [\text{NOx}]_{\text{out}}) / [\text{NOx}]_{\text{in}} \times 100 \%$$

where [NOx]=[NO] + [NO₂], and the subscripts “in” and “out” refer to the inlet and outlet concentration of NOx, respectively.

3. Results and discussion

3.1. SCR activity

A series of MnCe/MFA catalysts with different amount of Mn-Ce composite oxides at 2.5 wt%, 5 wt%, 7.5 wt%, 10 wt% and 12.5 wt% were prepared and their catalytic performance in SCR reaction were

given in Fig. 1. MnCe/MFA with Mn-Ce composite oxides loading at 5 wt% showed the highest NO conversion in the reaction temperatures of 250-350 °C. A NO conversion of 65% at 300 °C under a gaseous hourly space velocity (GHSV) of 50,000 h⁻¹ could be observed.

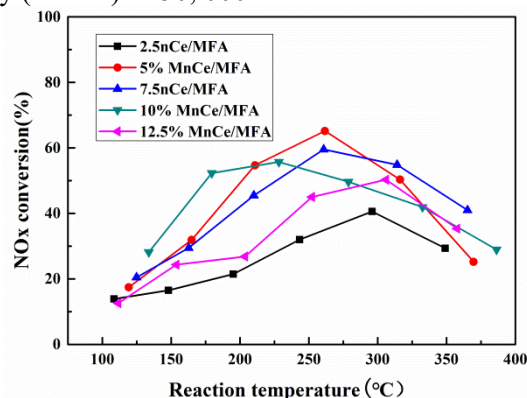


Fig. 1. NO_x conversion over MnCe/ MFA catalysts with different loading amount of Mn-Ce oxides. Reaction conditions: [NO] = [NH₃] = 700 ppm, [O₂] = 3.5 %, balance N₂, catalyst 0.5 g, and GHSV about 50 000 h⁻¹.

The effect of GHSV on NO_x conversion over 5%MnCe/MFA were investigated. As shown in Fig. 2, NO conversion was inversely related to GHSV. The NO conversion decreased slightly by about 5% with the GHSV increasing from 50000 h⁻¹ to 115000 h⁻¹. However, when the GHSV was decreased from 50000 h⁻¹ to 32857 h⁻¹, the NO conversion increased sharply by 30% approximately. A high NO conversion of 93% could be achieved at 300 °C under a GHSV of 32857 h⁻¹.

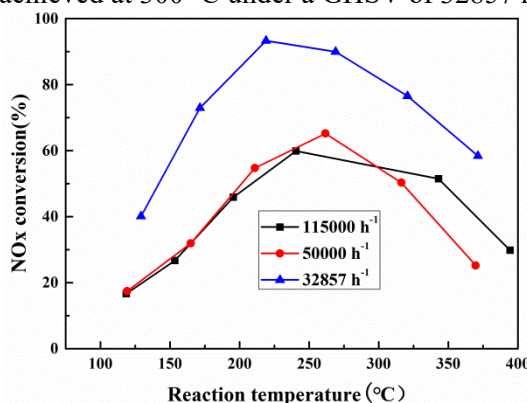


Fig. 2. Effect of GHSV on NO_x conversion over 5%MnCe/MFA. Reaction conditions: [NO] = [NH₃] = 700 ppm, [O₂] = 3.5 %, balance N₂, and GHSV about 50 000 h⁻¹.

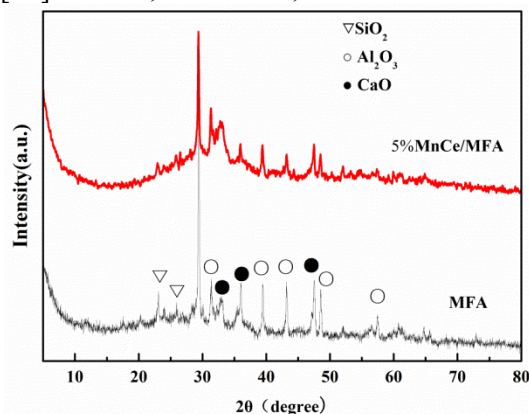


Fig. 3. X-ray diffraction spectra of MFA and 5%MnCe/MFA.

3.2. X-ray diffraction

X-ray powder diffraction was utilized to clarify the crystal phases of MFA and 5%MnCe/MFA. Diffraction peaks that ascribed to CaO (PDF#-28-0775), Al₂O₃ (PDF#-46-1215) and SiO₂ (PDF#-31-1234) could be observed on these two samples. In contrast, peak intensity of MnCe/MFA was lower than that of MFA, which revealed the strong interaction between Mn-Ce oxides and the MFA support. Diffraction peaks that belonged to Manganese or cerium compounds were hardly detected, demonstrating that the active species were highly dispersed on the surface of MFA and existed mainly in amorphous structure.

3.3. Physical characterizations

Table 1. BET specific surface area, total pore volume and mean diameter of samples.

Sample	S _{BET} (m ² /g)	Total pore volume (cm ³ /g)	Mean pore diameter (nm)
Raw fly ash	3.2	0.01	18.04
Modified fly ash	136.7	0.24	16.89
5%MnCe/MFA	44.3	0.15	17.29

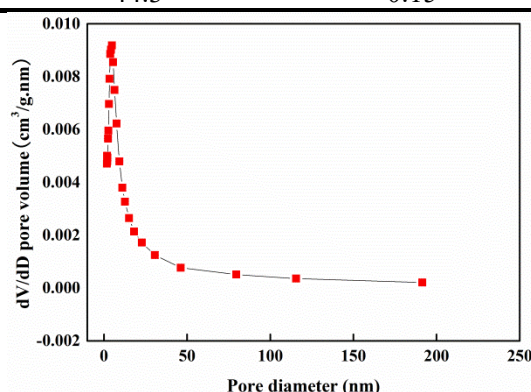


Fig. 4. Pore diameter distribution of 5%MnCe/MFA.

As displayed in Table 1, the hydrothermal treatment resulted in an obvious increasing of BET surface area and pore volume. As for raw fly ash, the BET surface area and pore volume were measured only at 3.2 m²/g and 0.01 cm³/g. However, both the BET surface area and pore volume of the modified fly ash increased greatly to 136.7 m²/g and 0.24 cm³/g. After the loading of Mn-Ce composite oxides, the BET surface area and pore volume decreased to a great extent, indicating that some pores were blocked by Mn-Ce composite oxides. The pore diameter distribution of 5%MnCe/MFA was shown in Fig. 4. Most of the pores diameters located at 2-50 nm, which meant 5%MnCe/MFA could be classified as mesoporous material.

3.4. Microstructure

Microstructure of 5%MnCe/MFA was observed by SEM and TEM. As shown in Fig. 5, different sized particles like stones could be seen in the SEM images, originated from the component of fly ash. A layer of small particle powders that ascribed to Mn-Ce composite oxides lay on the catalyst surface, which was further testified by the TEM images. In the high resolution TEM images, some small particles could be observed on the catalyst surface.

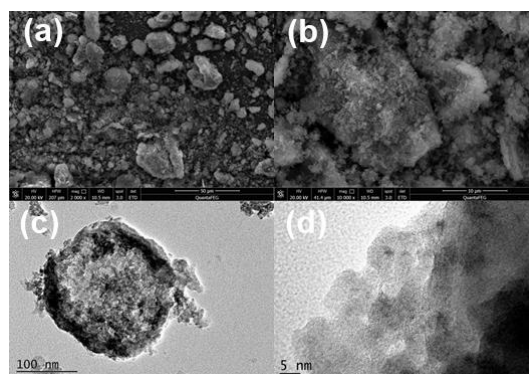


Fig. 5. SEM and TEM images of 5%MnCe/MFA.

3.5. X-ray photoelectron spectroscopy analysis

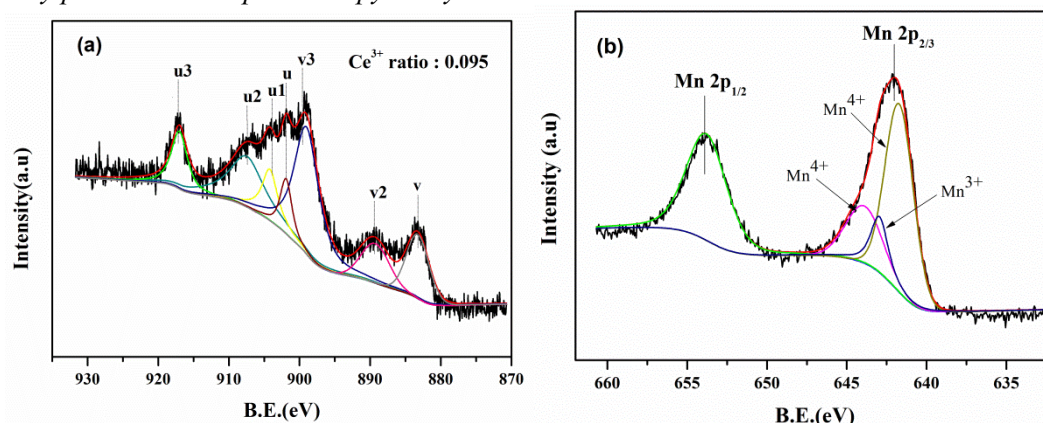


Fig. 6. Fitted Ce 3d and Mn 2p XPS spectra of 5%MnCe/MFA.

The 5%MnCe/MFA sample was further analyzed by XPS to identify the surface nature of various elements. The XPS spectrum of electronic state of cerium of 5%MnCe/MFA was shown in Fig. 6(a). The peaks labeled u, u2, u3, v, v2 and v3 represent the $3d^{10}4f^0$ state of Ce^{4+} ions, while the bands labeled u1 and v1 represent the $3d^{10}4f^1$ initial electronic state corresponding to Ce^{3+} .^[4, 5] It is reported that Ce^{3+} came from the ceria defects and accompanied by the formation of oxygen vacancies.^[6-8] The presence of Ce^{3+} species and oxygen vacancies could create a charge imbalance and unsaturated chemical bonds, which led to the increase of chemisorbed oxygen on the catalyst surface and promoted the repeatable Ce^{4+}/Ce^{3+} redox cycles in the final.^[6, 8, 9] On the contrary, the Ce^{4+}/Ce^{3+} redox cycles were seriously restrained once Ce^{3+} disappeared.^[8] It could be seen from Fig. 6 (a) that Ce^{3+} and Ce^{4+} were coexisted in the surface of 5%MnCe/MFA with a ratio of Ce^{3+} at 0.095, which was beneficial to obtaining a good catalytic activity.^[10, 11] Fig. 6 (b) showed the fitted XPS spectra of the Mn 2p. The peaks at approximately 641.7 eV and 642.9 eV arised from Mn 2p_{3/2}, and the peak at approximately 653.8 eV was from Mn 2p_{1/2}. According to the previous research, the binding energy at 641.7 eV and 642.9 eV could be attributed to Mn^{3+} of Mn_2O_3 and Mn^{4+} of MnO_2 , respectively.^[12, 13]

XPS analysis revealed that the chemical state of Mn-Ce composite oxides on the surface of 5%MnCe/MFA was quite diverse, which contributed to the good SCR activity of 5%MnCe/MFA.

3.6. Temperature programmed reduction analysis

The reducibility of 5%MnCe/MFA, 7% MnCe/MFA and 10% MnCe/MFA was investigated by H_2 -TPR. As shown in Fig. 7, two distinct reduction peaks could be observed on these three catalysts. The low temperature peaks at were ascribed to the reduction of manganese oxides, while the high temperature peaks were belonged to the reduction of cerium oxides.^[12, 14] The reduction of manganese

oxides started at a low temperature of 210 °C, suggesting the activeness of manganese oxides. Relatively speaking, the manganese oxides on 5%MnCe/MFA that showing a reduction peak at 386.6 °C was easier to be reduced than the other two catalysts, which accorded well with its best SCR activity showing in Fig. 1.

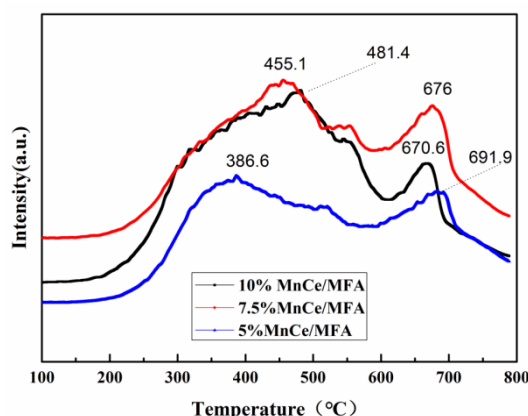


Fig. 7. H₂-TPR profiles of MnCe/MFA catalysts.

4. Conclusions

In this work, fly ash from municipal solid waste incineration was modified by hydrothermal treatment and became a good catalyst support for Mn-Ce composite oxides that using in SCR reaction. The prepared catalyst showed a high NO conversion of 93% at 300 °C under a GHSV of 32857 h⁻¹. Characterizations revealed that hydrothermal treatment brought a large surface area and abundant mesoporous to the modified fly ash, Mn-Ce composite oxides were highly dispersed on the surface of the support, and the chemical state of Mn-Ce composite oxides on the surface of 5%MnCe/MFA was quite diverse and showed a good redox property. These properties were the intrinsic reasons for the good SCR activity. This work transformed fly ash into high value-added products, providing a new approach to the resource utilization and pollution control of fly ash.

Acknowledgements

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References

- [1] Ferreira C, Ribeiro A and Ottosen L 2003 *Journal of Hazardous materials* **96** 201
- [2] Yang G C C and Yang T-Y 1998 *Journal of Hazardous materials* **62** 75
- [3] Bayuseno A P, Schmahl W W and Müllejans T 2009 *Journal of Hazardous materials* **167** 250
- [4] Beche E, Charvin P, Perarnau D, Abanades S and Flamant G 2008 *Surface and Interface Analysis* **40** 264
- [5] Larachi F, Pierre J, Adnot A and Bernis A 2002 *Applied Surface Science* **195** 236
- [6] Campbell C T and Peden C H F 2005 *Science* **309** 713
- [7] Esch F, Fabris S, Zhou L, Montini T, Africh C, Fornasiero P, Comelli G and Rosei R 2005 *Science* **309** 752
- [8] Dutta P, Pal S, Seehra M S, Shi Y, Eyring E M and Ernst R D 2006 *Chemistry of Materials* **18** 5144
- [9] Liu X, Zhou K, Wang L, Wang B and Li Y 2009 *Journal of the American Chemical Society* **131** 3140

- [10] Wang P, Wang H, Chen X, Liu Y, Weng X and Wu Z 2015 *Journal of Materials Chemistry A* **3** 680
- [11] Chen X, Gao S, Wang H, Liu Y and Wu Z 2011 *Catalysis Communications* **14** 1
- [12] Cao F, Xiang J, Su S, Wang P, Hu S and Sun L 2015 *Fuel Processing Technology* **135** 66
- [13] Qu L, Li C, Zeng G, Zhang M, Fu M, Ma J, Zhan F and Luo D 2014 *Chemical Engineering Journal* **242** 76
- [14] Wang H, Chen X, Gao S, Wu Z, Liu Y and Weng X 2013 *Catalysis Science & Technology* **3** 715