Available online at www.sciencedirect.com

ScienceDirect

Procedia Engineering 121 (2015) 952 – 956

Procedia Engineering

www.elsevier.com/locate/procedia

9th International Symposium on Heating, Ventilation and Air Conditioning (ISHVAC) and the 3rd International Conference on Building Energy and Environment (COBEE)

Design and Synthesis Functional Selective Catalytic Reduction Catalyst for NOx Removal

Zhenchao Fu[a,b], Mingyu Guo[a,b], Caixia Liu[a,b], Na Ji[a,b], Chunfeng Song[a,b], Qingling Liu[a,b] *

[a]*Tianjin Key Laboratory of Indoor Air Environmental Quality Control, School of Environmental Science and Engineering, Tianjin University,Weijin Road 92, Tianjin 300072, China*

[b]*State Key Laboratory of Engines, Tianjin University, Tianjin 300072, China*

Abstract

MeOx-Cu-SSZ-13 (Me=Mn, Ce) was synthesized by physically mixing mental oxide and ion-exchanged zeolite. The composite catalyst showed highly efficient for the NOx removal using NH3-SCR method. And the NO conversion is 98% for MnOx-CeO2/Cu-SSZ-13 at 150 °C and 97% for MnOx/Cu-SSZ-13 at 175 °C. Meanwhile, the N2 selectivity remains more than 98%. The catalysts are characterized by using XRD and SEM. The XRD patterns show that all samples are highly crystallized and without impurities. The SEM demonstrates all samples have uniform crystal size. Composite catalyst especially combined with Cu-SSZ-13 has considerable potential as a catalyst in the area of NOx conversion.

Peer-review under responsibility of the organizing committee of ISHVAC-COBEE 2015

Keywords: MeOx-Cu-SSZ-13; NH_3-SCR NOx; Catalyst

1. Introduction

Nitrogen oxides (NOx) are considered to be major air pollutant which can result a series of devastating effect on the ecosystem, human health and the atmosphere[1,2,3,4]. 90% of NOx emissions is from fossil fuel combustion. According to the type of pollution source, it can be divided into stationary and mobile sources. Stationary sources are mainly thermal power plants and industrial boilers, and mobile sources are mainly gasoline and diesel engines[5]. Among all kinds of NOx removal strategies, NH_3-SCR of NOx is the most mature and efficient technology for

* Corresponding author. Tel.: +86-02287401255.; fax: +86-02287401255..
E-mail address: Liuql@tju.edu.cn

Peer-review under responsibility of the organizing committee of ISHVAC-COBEE 2015
doi:10.1016/j.proeng.2015.09.061

decreasing NOx. The technology has been widely used in Coal-fired boiler, vehicle exhaust and even the future marine exhaust[6]. The principle is that adding NH_3 as reducing agent, and reduce NOx into harmless N_2 selectively. The equation is as follows:

Standard SCR reaction：$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O$ [7]

Fast SCR reaction：$4NH_3 + 2NO + 2NO_2 \rightarrow 4N_2 + 6H_2O$[7]

The key of the NH_3-SCR technology is to develop highly efficient and stable catalyst. Vanadium supported on titanium with WO_3 or MoO_3 as promoters is the mainly commercial catalyst in industrial applications[8]. The catalyst has a highly catalytic activity in the temperature range of 350-400 ° C, but it still remains some problems. For example, the catalyst contains toxic substances V_2O_5, which has a biological toxicity to the environment. The catalyst system also has some shortcomings including narrow operating temperature window, generating a lot of greenhouse gas N_2O at high temperature and poor thermal stability[9,10]. People have committed to the development of novel high NH_3-SCR activity, wide operating temperature window, hydrothermally stable and environmentally friendly catalyst system.

Currently, more researches are mainly focus on metal oxide catalysts (especially Mn, Ce-based metal oxide catalysts) and metal-ion-exchanged zeolite catalysts (especially Fe, Cu-based zeolite catalysts) [11,12]. Due to the high NH_3-SCR performance at low temperature, Mn-based oxide catalyst received extensive attention. Tang et al. have prepared MnOx catalysts through various methods such as co-precipitation, low temperature solid phase reaction and rheological phase reaction. The NOx conversion can reach 90% at 80 ° C, and the NOx conversion reach nearly 100% at 100 ~ 150 ° C[13]. However, there are still some drawbacks like poor resistance to H_2O and SO_2. Moreover, it has been reported that MnOx-CeO_2 catalyst show higher catalytic activity which the N_2 selectivity get to 100% at 100-150°C[14]. This result confirms that composite oxide catalysts are of great interest due to one metal element can modify the catalytic properties of another.

Recently, the NH_3-SCR catalyst supported on CHA structure zeolite has received extensive attention because of the high activity, good thermal stability, good anti-HC poisoning performance. Kwak et al. Compared the activity of Cu-SSZ-13,Cu-ZSM-5 and Cu-beta, and Cu-SSZ-13 was found not only the best catalytic activity and a very good N_2 selectivity, but also has minimum amount of by-product including NO_2 and N_2O[15]. But we also need to face the challenge of hydrothermal stability of the catalyst.

To the best of our knowledge, the combination of MeOx and Cu-SSZ-13 as a novel catalyst for NH_3-SCR of NOx has not been investigated yet. Herein, we report the synthesis of the composite catalysts and demonstrate their activity.

2. Methods

2.1. Preparation of catalysts

Cu-SSZ-13 was prepared by the ion-exchange method: $Cu(NO_3)_2{\cdot}3H_2O$ (12.08g), deionzed water（500 ml）. $Cu(NO_3)_2{\cdot}3H_2O$ was dissolved in deionized water to prepare $Cu(NO_3)_2$ solutions(0.1mol L^{-1}). H-SSZ-13(Si/Al=13.6) was mixed with the $Cu(NO_3)_2$ solutions. After stirringing the suspension under constant temperature at 80 ° C in the oil bath for 2 h, the samples were filrated and washed with deionized water, and then dried at 100°C for12 h.

MeOx-Cu-SSZ-13（Me=Mn,Ce）catalysts were prepared by a physical mixing method. The mixture was heating and stirring until the mixture become homogeneous, and then dried at 100°C for 12h and calcined in muffle.

2.2. Catalyst characterization

The catalysts structure were characterized by X-ray powder diffraction (XRD) (Rigaku D/MAX 2550) with Cu Kα radiation (λ=1.540598 Å), at 40 kv beam voltage , the scan range is from 5 to 90° with the scanning step:0.02°.The morphology of the catalysts were characterized by Scan electronic microscope (SEM)(JEOL JSM-6700F field-emission scanning microscope) with 200 kv accelerating voltage.

2.3. Catalyst activity tests

The catalytic activity test was carried out in a fixed-bed continuous evaluation system. 0.2 mg of catalyst was fixed in the middle of the quartz tube reactor supported by glass wool at the bottom. And the reactor was heated by an electric tubular furnace coupled with a thermocouple probe inserted to the catalyst bed to control the temperature. Activity evaluation criteria: 500 ppm NO, 500 ppm NH_3, 5 vol.% O_2, N_2 as balanced gas. FTIR spectrometer from MKS Instruments was used to measure the concentrations of all kinds of outlet reactant gas. The NO conversion and N_2 selectivity were calculated by equations (1) and (2) respectively:

$$(NOx)conversion = \left[1 - \frac{[NO]_{out} + [NO_2]_{out}}{[NO]_{in} + [NO_2]_{in}}\right] \times 100\% \quad (1)$$

$$(N_2)selectivity = \left[\frac{[NO]_{in} + [NH_3]_{in} - [NO_2]_{out} - 2[N_2O]_{out}}{[NO]_{in} + [NH_3]_{in}}\right] \times 100\% \quad (2)$$

3. Results and discussion

3.1. X-ray diddraction(XRD)

The XRD patterns demonstrate that all samples are highly crystallized and without impurities as shown in Figure 1. Comparing with standard card we can also found that the three samples all contain Cu-SSZ-13 species. And Mn species and Ce species can be observed in (a) and (b) respectively.

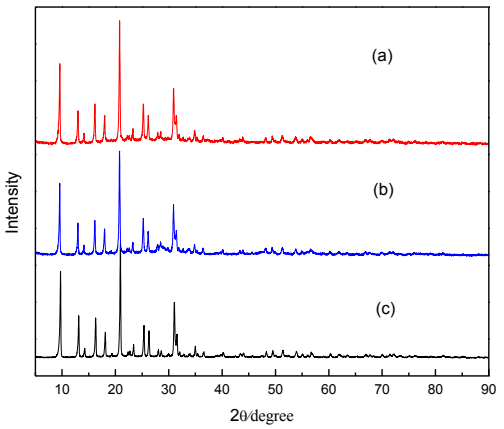

Fig. 1. XRD profiles of MnOx/Cu-SSZ-13 (a), MnOx-CeO2/Cu-SSZ-13 (b), Cu-SSZ-13 (c).

3.2. Scanning electron microscopy(SEM)

Figure 2 shows the SEM images of MnOx/Cu-SSZ-13,MnOx-CeO_2/Cu-SSZ-13 and Cu-SSZ-13. All samples have uniform crystal size, but if we compare (a) and (b) with (c), different morphologies for the two mixed MnOx/Cu-SSZ-13 and MnOx-CeO_2/Cu-SSZ-13 are observed with the mixed state of Cu-SSZ-13 and MeOx.

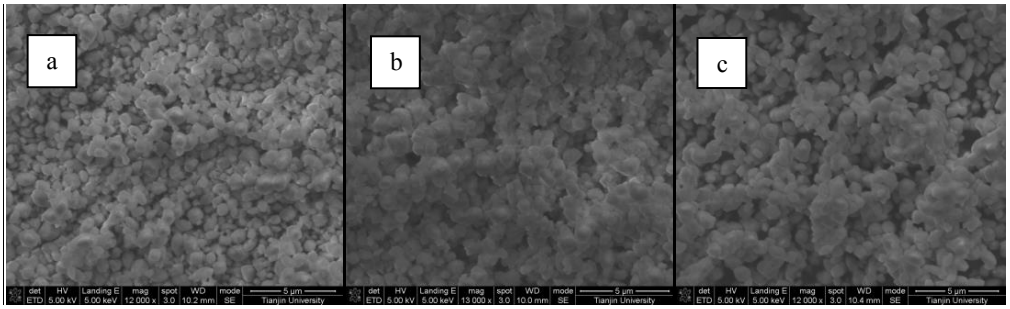

Fig. 2. SEM image of MnOx/Cu-SSZ-13(a), MnOx-CeO2/Cu-SSZ-13(b), Cu-SSZ-13(c)

3.3. SCR performance of different catalysts

NO conversions and N_2 selectivity as functions of reaction temperatures over MeOx-Cu-SSZ-13 (Me=Mn,Ce) are shown in Figure 3. The NOx conversions over the MeOx-Cu-SSZ-13 (Me=Mn,Ce) exceeded 80% at 100°C~200°C. And the catalytic activity of MeOx-Cu-SSZ-13 (Me=Mn,Ce) is superior to other catalysts. Clearly, MeOx-Cu-SSZ-13 (Me=Mn, Ce) enhances NO conversion remarkably compared with single MnOx, CeO_2 and Cu-SSZ-13.

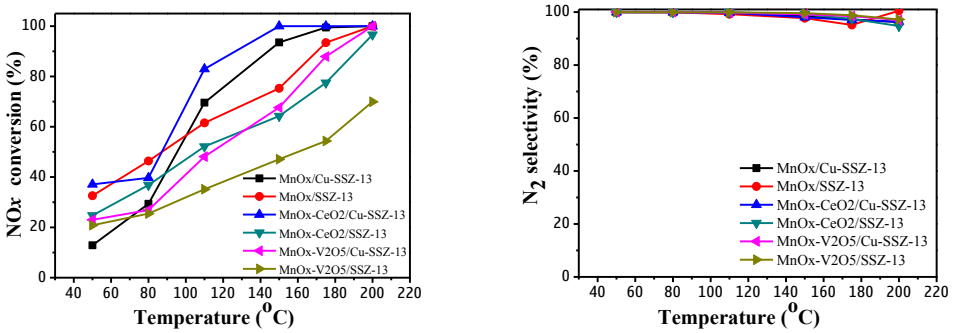

Fig. 3. Catalytic performance for SCR of NOx with ammonia on MnOx/Cu-SSZ-13(black), MnOx-CeO2/Cu-SSZ-13(blue).(0.05%NO, 0.05% NH_3, 3%O_2, N_2 balanced, 300ml/min, space rate:15000h-1, CeO_2+MOx(Wt%) =10%, CeO_2:MOx=2;3;V_2O_5 +MOx(Wt%) =10%, V_2O_5:MOx=2:3;)

4. Conclusion

In summary, we have developed a new environmentally friendly catalyst for NOx emission control. By physically mixing two excellent catalysts, we can get a more efficient composite catalyst. What we can know from the investigation is as following:

- The mixed catalysts are crystallized and have uniform crystal size.
- The composite catalyst is highly efficient, and the NO conversion are 98% for MnOx-CeO_2/Cu-SSZ-13 at 150 °C and 97% for MnOx/Cu-SSZ-13 at 175 °C . The N_2 selectivity remains more than 98% for these two catalysts.

Acknowledgements

This research was financially supported by the National Natural Science Fund of China (grant no. 21406165), Natural Science Fund of Tianjin and Special fund of State Key Laboratory of Engines.

References

[1] I.F. Roth, and L.L. Ambs, Incorporating externalities into a full cost approach to electric power generation life-cycle costing, Energy. 29.12 (2004) 2125-2144.
[2] S.D. Beevers, E. Westmoreland, M.C.D. Jong, Trends in NO x and NO 2 emissions from road traffic in Great Britain, Atmos. Environ. 54.5 (2012) 107–116.
[3] V. Grewe, K. Dahlmann, W.Steinbrecht, Attributing ozone to NO x emissions: Implications for climate mitigation measures. Atmos. Environ. 59.7 (2012) 102–107.
[4] S. A. Abdul-Wahab, M. Azzi, G. M. Johnson. Using the integrated empirical rate-reactive plume model in assessment of the potential effects of Shuaiba Industrial Area NOx plumes on photochemical smog concentrations. Process Safety & Environmental Protection 81.5 (2003) 363-374.
[5] P. Forzatti, L. Lietti, Pio. Forzatti, Recent Advances in De-NOxing Catalysis for Stationary Applications. Heterogeneous Chemistry Reviews. 3.1 (1996) 33-51.
[6] B.H. Engler, L. Robert, U. D. Balzo, Complement-Induced Myocardial Ischemia: Neutrophil and Vascular Mechanisms. Regulation of Coronary Blood Flow 1991.
[7] G. Busca, L. Lietti, G. Ramis, Chemical And Mechanistic Aspects Of The Selective Catalytic Reduction Of Nox By Ammonia Over Oxide Catalysts: A Review, Applied Catalysis B Environmental. 18.1-2 (1998):1–36.
[8] H. Bosch, and F. Janssen, Formation and Control of Nitrogen Oxides, Catal. Today. 2 (1988) 369-532.
[9] S. Roy, M.S. Hegde, G. Madras, Catalysis for NO x abatement, Appl. Energ. 86. 11 (2009) 2283–2297.
[10] V.I. Parvulescu, P. Grange, B. Delmon, Catalytic removal of NO, Catalysis Today volume. 46 (1998) 233-316(84).
[11] G. Busca, L. Lietti, G. Ramis, Chemical And Mechanistic Aspects Of The Selective Catalytic Reduction Of Nox By Ammonia Over Oxide Catalysts: A Review, Applied Catalysis B Environmental. 18.1-2 (1998) 1–36.
[12] S. Brandenberger, O. Krocher, A . Tissler, et al. "The State of the Art in Selective Catalytic Reduction of NOx by Ammonia Using Metal-Exchanged Zeolite Catalysts, Catalysis Reviews. 50.4 (2008) 492-531(40).
[13] X.G. Tang, Q.X. Liu, L.L.Jiang, Optical properties of Pb(ZrxTi161x)O3 (x=0.4, 0.6) thin films on Pt-coated Si substrates studied by spectroscopic ellipsometry, Materials Chemistry & Physics 103. 103 (2007) 329–333.
[14] G. Qi, R.T. Yang, R. Chang, MnO x -CeO 2 mixed oxides prepared by co-precipitation for selective catalytic reduction of NO with NH3 at low temperatures. Applied Catalysis B Environmental. 51.2 (2004) 93–106.
[15] J. H. Kwak, R.G. Tonkyn, D.H. Kim, Excellent Activity And Selectivity Of Cu-Ssz-13 In The Selective Catalytic Reduction Of Nox With NH3, Journal of Catalysis. 275.2 (2010) 187–190.