MnO_x-CeO_2 supported on Cu-SSZ-13: A novel SCR catalyst in a wide temperature range

Qingling Liu[a], Zhenchao Fu[a], Lei Ma[d], Caixia Liu[a,c*], Junhua Li[b], Ziyin Zhang[c].
[a]School of Environmental Science and Engineering, Tianjin University, Tianjin, 300072, China
[b] State Key Joint Laboratory of Environment Simulation and Pollution Control, School of Environment, Tsinghua University, Beijing 100084, China
[c]Langfang city Beichen Entrepreneurship Resin Materials Company, Hebei province 065000,China
[d]Department of Chemical Engineering, University of Michigan, MI 48824, USA
[e]School of Energy and Environmental Engineering, Hebei University of Technology, Tianjin 300401, China
[a*]Corresponding author. Tel. ++86 22 87402072, Fax : ++86 22 27407956, E-mail address:liucx@tju.edu.cn

Abstract:

A novel Mn-Ce/Cu-SSZ-13 catalyst was synthesized and The NO_x conversions of this catalyst showed good H_2O and SO_2 resistances at 300°C and possessed higher activities than Cu-SSZ-13 at 80 °C to 175 °C and Mn-Ce at above 200°C. NH_3 was easily adsorbed to form NH_4NO_3on Cu-SSZ-13 , which encased the surface of the catalyst, thereby blocking the pores and deactivating the active sites. However, for Mn-Ce/Cu-SSZ-13, the bridging nitrates were adsorbed onto the surface and then converted to monodentate nitrates, which acted as the active species for the SCR reaction at low temperature.

Keywords: NH_3-SCR, low temperature, synergistic interaction.

1. Introduction

Selective catalytic reduction of NO by NH_3 (NH_3-SCR) is the most popular NO_x removal technology that has been widely applied in controlling NO_x exhaust from diesel engines, marine engines, and coal-fired boilers[1–3].The core aspect of NH_3-SCR technology is the catalyst. V_2O_5/WO_3 and V_2O_5/MoO_3 are the primary commercial catalysts that have been widely applied in stationary and mobile areas [4–5]. These catalysts exhibit excellent SCR performances at 340 °C to 400 °C but poses several disadvantages, such as toxicity, high activity for oxidizing SO_2 to SO_3, and a narrow reaction temperature range [6–8]. Many researchers have developed a low-temperature catalyst (below 250 °C) that works well downstream of the electrostatic precipitator and desulfurizer in power plants [9,10] and can also efficiently remove NO_x in a wide temperature range in diesel engines [11]. Herein, a novel Mn-Ce/Cu-SSZ-13 catalyst with excellent NH_3-SCR performance in a wide temperature range was developed. The catalyst was characterized by XRD, BET, SEM, H_2-TPR, NH_3-TPD, NO+O_2-TPD, and in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). Compared with pure Cu-SSZ-13, Mn-Ce/Cu-SSZ-13 exhibited an excellent SCR performance at low temperature. The reactivities of surface-adsorbed NH_3 and NO_x species on the two catalysts were investigated. We proposed a possible reaction pathway over the Mn-Ce/Cu-SSZ-13 catalyst and provided an explanation for the desirable low-temperature SCR performance of the Mn-Ce/Cu-SSZ-13.

2. Experimental (or Theoretical)

Cu-SSZ-13 was prepared by a conventional aqueous solution ion-exchange method. $Cu(NO_3)_2 \cdot 3H_2O$ (12.08g) was dissolved in deionized water (500 ml) to prepare $Cu(NO_3)_2$ solutions (0.1molL^{-1}). H-SSZ-13(Si/Al=13.6) was added into the $Cu(NO_3)_2$ solutions. Stirred the solution at 80 ° C in the oil bath for 2 h, and then washed the product with deionized water. At last, the product was dried at 100°C for12 h.

The Mn-Ce/Cu-SSZ-13 catalyst was prepared with an impregnation method. Firstly, 1.34g of manganese nitrate and 0.45 g of cerium nitrate were dissolved into 15.00 g deionized water. After then, 4.00 g of Cu-SSZ-13 was introduced to the Mn-Ce solution and the resulting solution was stirred by magnetic for 1 h. The paste was dried at 100 °C overnight and calcined at 550°C for 4 min in muffle. The mole ratio of MnO_x: CeO_2:Cu-SSZ-13 in the catalyst was 6:4:90.

3. Results and discussion

As shown in Fig. 1a and Fig. 1b, the Mn-Ce, Cu-SSZ-13 and Mn-Ce/Cu-SSZ-13 catalysts were prepared and tested. The NO_x conversions as a function of reaction temperature between 50 and 500°C on the Mn-Ce, Cu-SSZ-13 and Mn-Ce/Cu-SSZ-13 catalysts are shown in Fig. 1a. The temperature window for a NO_x removal efficiency exceeding 90% over Cu-SSZ-13 was 175~500°C, and the NO_x conversion of Mn-Ce reached up to 90% from 110 to 200°C and then decreased steadily from 83% to -61% from 250 to 500°C. Amazingly, after doping with MnO_x and CeO_2, the NO_x conversion of Mn-Ce/Cu-SSZ-13 was above 90% from 125~450°C. As shown in Fig. 1b, the N_2 selectivity of the Mn-Ce/Cu-SSZ-13 and Cu-SSZ-13 catalysts was retained at 90% in the entire temperature window, but for the Mn-Ce catalyst, it decreased gradually from 98% to 18% with an increasing temperature up to 300°C and then rapidly increased to 80% at 500°C. These results demonstrated that Mn-Ce/Cu-SSZ-13 possessed higher activity than Cu-SSZ-13 at low temperatures and higher activity than Mn-Ce at high temperatures, indicating that the Mn-Ce/Cu-SSZ-13 catalyst is a promising catalyst in a wide temperature window.

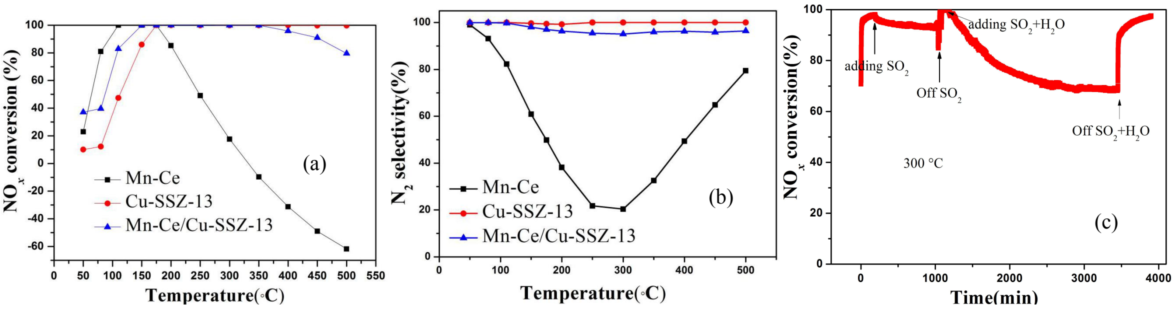

Fig. 1. Performances for SCR of NO_x with NH_3 on the catalysts: (a) NO_x conversions on MnO_x-CeO_2, Cu-SSZ-13 and Mn-Ce/Cu-SSZ-13, (b) N_2 selectivities on MnO_x-CeO_2, Cu-SSZ-13 and Mn-Ce/Cu-SSZ-13, (c) SO_2 and H_2O resistances on Mn-Ce/Cu-SSZ-13 (300°C, 3% H_2O). Reaction conditions: [NO] = [NH_3] = 500 ppm, [O_2] = 3%, N_2 balance, total flow rate = 300 mL min^{-1} and GHSV = 50,000 h^{-1}.

4. Conclusions

In this study, the promotional effects of adding MnO_x-CeO_2 into Cu-SSZ-13 were investigated. Results showed that the Mn-Ce/Cu-SSZ-13 catalyst exhibited superior catalytic activity for the SCR of NO by ammonia in a wide temperature range of 125–450 °C and with a high resistance to H_2O+SO_2 poisoning at 300 °C. The factors leading to the promotional effects from doping MnO_x–CeO_2 should be considered to obtain a deep understanding on how to improve the SCR activity through doping of MnO_x–CeO_2 into Cu-SSZ-13.

The addition of MnO_x–CeO_2 did not affect the small pore size of CHA but decreased the surface area and pore volume. TPD and in situ DRIFTS analyses showed that bridging nitrate groups on Cu-SSZ-13 could not participate in the SCR reaction. Moreover, NH_3 was easily adsorbed to form NH_4NO_3, which encased the surface of the catalyst, thereby blocking the pores and deactivating the active sites. However, for Mn-Ce/Cu-SSZ-13, the bridging nitrates were adsorbed onto the surface and then converted to monodentate nitrates, which acted as the active species for the SCR reaction at low temperature. This phenomenon might be the primary reason for the enhanced SCR performance of Mn-Ce/Cu-SSZ-13 compared with Cu-SSZ-13 at low temperature.

Acknowledgements

This work was financially supported by the National Natural Science Fund of China (Grant No. 21507100 and No. 21406165) and the National High-Tech Research and Science and Technology Plan Program of Hebei Province (Grant No. 16274006D).

References

1. P. Forzatti, Catal. Today, 62 (2000) 51-65.
2. W.S.D.P. Fudong Liu, Chinese J.Catal., 35 (2014) 1438-1445.
3. M. Magnusson, E. Fridell, H.H. Ingelsten, Appl.Catal. B, 111-112 (2012) 20-26.
4. G. Busca, L. Lietti, G. Ramis, F. Berti, Appl.Catal. B, 18 (1998) 1-36.
5. J. Li, H. Chang, L. Ma, J. Hao, R.T. Yang, Catal. Today, 175 (2011) 147-156.
6. J.P. Dunn, P.R. Koppula, H.G. Stenger, I.E. Wachs, Appl.Catal. B, (1998).
7. R.Q. Long, R.T. Yang, J. Am. Chem. Soc.,121 (1999) 5595-5596.
8. K. Rahkamaa-Tolonen, T. Maunula, M. Lomma, M. Huuhtanen, R.L. Keiski, Catal. Today, 100 (2005) 217-222.
9. G. Qi, R.T. Yang, J.Catal, 217 (2003) 434-441.
10. H.B.F. Janssen, Catal. Today, (1988) 366-369.
11. J.H. Kwak, D. Tran, J. Szanyi, C.H.F. Peden, J.H. Lee, Catal.Lett., 142 (2012) 295-301.