Promoted NH_3-SCR catalytic performance and hydrothermal stability by the addition of tungsten species to CeZrOx mixed oxides

Jingjing Liu,[a] Xiaoyan Shi,[a] Hong He[a]*

[a] *Research Center for Eco-environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China*

** Fax: +86 10 62849123. honghe@rcees.ac.cn*

Abstract: A series of tungsten doping CeZrOx mixed oxides catalysts prepared by homogeneous precipitation method showed high NH_3-SCR activity and excellent hydrothermally stability. The textural property, redox ability and acid sites on the fresh and hydrothermal aged tungsten doping CeZrOx mixed oxides were systematically characterized using various methods including N_2 physisorption, Raman, XRD, H_2-TPR, XPS and *in situ* DRIFTs. The results showed that the excellent catalytic performance of tungsten doping CeZrOx is related to the improved structural properties and acid sites by the addition of tungsten.

Keywords: NH_3-SCR, Hydrothermal stability, Tungsten-cerium-zirconium.

1. Introduction

The selective catalytic reduction (SCR) of NOx by NH_3 (NH_3-SCR) is one of the most efficient method for NOx removal from diesel engines. Since diesel particle filters (DPFs) are often placed upstream of the SCR catalyst and the regeneration of DPFs could put NH_3-SCR catalyst into high temperature and high humidity environment, the hydrothermal stability of SCR catalysts at high temperatures is very important for the practical applications. Pure CeO_2 is susceptible to be sintered at high temperature and the hydrothermal stability of the Ce based SCR catalysts are questionable for practical application for the diesel after treatment systems.[1] The introduction of ZrO_2 to CeO_2 could effectively improve the thermal stability of CeO_2.[2] It needs to be emphasized that tungsten species are extremely effective addition agent for the promotion of NH_3-SCR activity.[3] In this work, the structure-activity relationships for a series of W-doping $Ce_1Zr_1O_x$ catalysts and the mechanisms of hydrothermal aging were studied.

2. Experimental

The $Ce_1W_aZr_1O_x$ (a=0.3, 0.5, 0.9) and $Ce_1Zr_1O_x$ catalysts were synthesized by homogeneous precipitation method using urea as the precipitator. The fresh catalysts were hydrothermally aged in the air containing 10 vol.% H_2O at 700°C, 750°C, 800°C and 850°C for 16h with a GHSV of 70,000 h^{-1} and were denoted as $Ce_1W_{0.5}Zr_1O_x$-t and $Ce_1Zr_1O_x$-t, where "t" represents the hydrothermally-aging temperature. The NH_3-SCR activity measurements of the catalysts were carried out in a fixed-bed quartz tube flow reactor with inner diameter of 4mm. The flue gas compositions were as follows: 500ppm NO, 500ppm NH_3, 5%O_2, balance N_2. Reactant gases were regulated by mass-flow controllers before entering the reactor. The inlet and outlet concentrations of NH_3, NO, NO_2 and N_2O were continually monitored by FTIR spectrometer (IS10 Nicolet) which was equipped with a multiple path gas cell (2m).

3. Results and discussion

Figure 1(a) shows the NOx conversion of $Ce_1W_aZr_1O_x$ (a = 0.3, 0.5, 0.9) in comparison to the $Ce_1Zr_1O_x$ under a GHSV of 250,000h^{-1}. It can be seen that, the SCR activity of $Ce_1Zr_1O_x$ was relatively low and the maximum NO conversion of this catalyst was only 74% in the operating temperature range. The addition of W into $Ce_1Zr_1O_x$ significantly increased the SCR activity. The low-temperature activity was improved with increasing the W/Ce molar ratio from 0.3 to 0.5. However, when further increasing the W doping amount, the NOx conversion of $Ce_1W_{0.9}Zr_1O_x$ decreased at temperature below 300°C. The $Ce_1W_{0.5}Zr_1O_x$ which showed the best SCR activity in fresh catalysts was selected for the investigation of hydrothermal stability of $Ce_1W_aZr_1O_x$. Figure 1(b) shows the NOx conversion of $Ce_1W_{0.5}Zr_1O_x$ after hydrothermal aging at different temperatures for 16h. An obvious decrease of the low temperature activity and slight enhancement of high temperature activity were observed for $Ce_1W_{0.5}Zr_1O_x$ after hydrothermal aging at 700°C. Furthermore, the loss of low temperature activity increased with the increasing hydrothermal

aging temperature. It is worth noting that, after severe hydrothermal aged at 850°C for 16h, $Ce_1W_{0.5}Zr_1O_x$ still exhibited higher NH_3-SCR activity compared to fresh $Ce_1Zr_1O_x$. The NOx conversion of $Ce_1W_{0.5}Zr_1O_x$-850 was more than 80% in the temperature range from 300-500°C. It suggests that $Ce_1W_{0.5}Zr_1O_x$ showed excellent hydrothermal stability.

Figure 2(a) shows the XRD results of CeO_2, ZrO_2, $Ce_1Zr_1O_x$ and $Ce_1W_{0.5}Zr_1O_x$. It shows that the main peaks in XRD pattern of $Ce_1W_{0.5}Zr_1O_x$ were attributed to the *c*-CeO_2 and no XRD diffraction peaks assigned to tungsten oxides and zirconium oxide can be detected. The XRD patterns of $Ce_1W_{0.5}Zr_1O_x$ and $Ce_1W_{0.5}Zr_1O_x$-t were displayed in Figure 2(b). It can be seen that the characteristic diffraction peaks of *c*-CeO_2(PDF 43-1002), *t*-$Zr_{0.84}Ce_{0.16}O_2$(PDF 38-1437) and $Ce_4W_9O_{33}$ (JCPDS 25-0192) appeared over $Ce_1W_{0.5}Zr_1O_x$-700 catalyst, indicating that the occurrence of phase segregation after the hydrothermal-aging at 700°C for 16h. Additionally, compared with $Ce_1W_{0.5}Zr_1O_x$-700, little change of XRD patterns can be observed for the samples which were hydrothermal treated at higher temperatures.

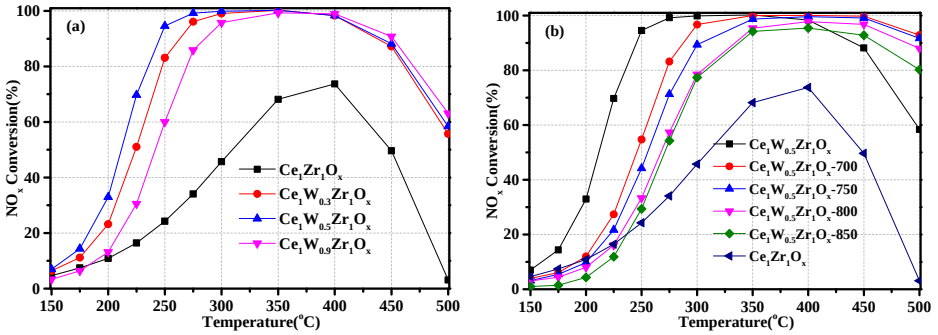

Figure 1. The effects of W doping amount (a), and hydrothermal-aging temperature (b) on the NOx conversion over catalysts. Reaction conditions: [NO] = [NH_3] = 500 ppm, [O_2] = 5 vol.%, balance N_2, GHSV = 250,000h^{-1}.

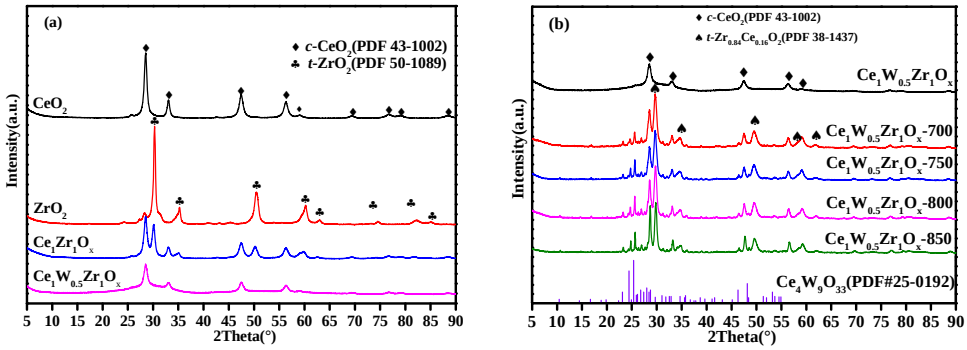

Figure 2. Powder XRD of fresh (a) and hydrothermally-aging catalysts (b).

4. Conclusions

A series of $Ce_1W_aZr_1O_x$ catalysts which were synthesized by homogeneous precipitation show high activity in the NH_3-SCR reaction. The optimized sample, $Ce_1W_{0.5}Zr_1O_x$ showed most excellent NH_3-SCR activity and remarkable hydrothermal stability. It was found that, the doping of W into $Ce_1Zr_1O_x$ influenced the crystallization of Ce and Zr in the bulk, which resulted in more appropriate texture for NH_3-SCR reaction. The $Ce_1W_{0.5}Zr_1O_x$ showed high hydrothermal stability. Even after hydrothermal aging at 850°C for 16h, 80% NOx conversion can be reached in the temperature range from 300-500°C for $Ce_1W_{0.5}Zr_1O_x$.

References

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