A CeO₂/ZrO₂-TiO₂ catalyst for the selective catalytic reduction of NOₓ with NH₃

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Abstract: A CeO₂/ZrO₂-TiO₂ catalyst was prepared by a stepwise precipitation approach for the selective catalytic reduction of NOₓ with NH₃. Through the control of pH value and precipitation time during preparation, the function of the CeO₂/ZrO₂-TiO₂ catalyst could be controlled and the structure with highly dispersed CeO₂ (with redox functions) on the surface of the ZrO₂-TiO₂ (with acidic functions) could be obtained. Characterizations revealed that the obtained CeO₂/ZrO₂-TiO₂ catalyst could exhibit superior redox functions, outstanding adsorption and activation properties for NOₓ and NH₃, and enhanced charge imbalance, which is the main reason for the excellent catalytic performance of the catalyst.

Keywords: Ce-based catalyst, selective catalytic reduction, diesel exhaust.

1. Introduction

Selective catalytic reduction of NOₓ with NH₃ (NH₃-SCR) has been widely applied for the removal of NOₓ generated from stationary sources for many years, and it has also become the dominant technology for the control of NOₓ emission from diesel vehicles.¹ There have been strong interests in developing vanadium-free catalyst NH₃-SCR catalysts with excellent catalytic performance for diesel vehicles.²⁻⁴ In the NH₃-SCR reaction, both redox functions and acidic functions of the catalyst are needed. Therefore, highly disperse of active sites and close coupling of redox with acid sites are the key factors for the design of a high efficiency NH₃-SCR catalyst.

2. Experimental

The CeO₂/ZrO₂-TiO₂, with a Ce/Zr/Ti molar ratio of 1:0.5:2, was prepared by a precipitation method. The reaction was performed on a fixed-bed quartz flow reactor. The effluent gas, including NO, NH₃, NO₂ and N₂O, was continuously analyzed by an online FTIR gas analyzer (Nicolet Antaris IGS analyzer). Characterization methods, including XRD, XPS, H₂-TPR, NOₓ-TPD, and NH₃-TPD, were used to investigate the catalyst.

3. Results and discussion

Due to the strong acidity of the added Ti(SO₄)₂ (as the precursor of the Ti), the initial pH of the mixed solution during the preparation of CeO₂/ZrO₂-TiO₂ dropped to be 1.1. After heating, the pH of the solution increased gradually due to the hydrolysis of urea, and some white suspended particles were produced in the first hour. After 4 hours of reaction, the pH of the solution increased to be 6.1 and the suspended particles turned to be light yellow. After 12 hours of heating, the pH reached ca. 7.0 and the color of the suspended particles was yellow. The particles with different precipitation time (1 h, 4 h, 6 h, and 12 h) were collected and then prepared to be catalyst samples. Interestingly, the activity test showed a remarkably enhancement of the NOₓ conversions over the samples with the increase of precipitation time (Figure 1).

The surface metal atomic concentrations of the samples with different precipitation times were analyzed by XPS, and the variations of Ce, Zr, and Ti concentrations with precipitation time were shown in Figure 2. On the sample of 1 h precipitation, just Ti and Zr, without Ce, were detected. With the increase of precipitation time, the samples showed a gradually increase of surface Ce concentration. At the same time,
both of the surface Ti and Zr concentrations gradually decreased with the increase of precipitation time. Considering the variation of the solution pH during the preparation, the formation process of the CeO$_2$/ZrO$_2$-TiO$_2$ can be proposed as follows: the Ti and Zr species were firstly co-precipitated when the pH of the mixed solution increased, and then the Ce species was precipitated uniformly onto the precipitated Zr-Ti species due to the further increase of pH. Finally, a CeO$_2$/ZrO$_2$-TiO$_2$ catalyst with higher surface Ce concentration than Ti and Zr was obtained. Through the control of the hydrolysis of urea, the variation of the solution pH can be controlled, and then we can control the precipitation process, which is very important for the formation of highly dispersed CeO$_2$ on ZrO$_2$-TiO$_2$. Thus, the obtained catalyst can present excellent NH$_3$-SCR performance.

Characterizations, including XRD, XPS, H$_2$-TPR, NO$_x$-TPD, and NH$_3$-TPD, were carried out for the CeO$_2$/ZrO$_2$-TiO$_2$, and this catalyst showed superior redox functions, outstanding adsorption and activation properties for NO$_x$ and NH$_3$, and enhanced charge imbalance.

4. Conclusions

In this study, a CeO$_2$/ZrO$_2$-TiO$_2$ catalyst, with highly dispersed CeO$_2$ (with redox functions) on the surface of the ZrO$_2$-TiO$_2$ (with acidic functions), was developed for the NH$_3$-SCR. The catalyst showed superior redox functions, outstanding adsorption and activation properties for NO$_x$ and NH$_3$, and enhanced charge imbalance. Thus, it exhibited excellent NH$_3$-SCR performance.

References