# A $CeO_2/ZrO_2$-$TiO_2$ catalyst for the selective catalytic reduction of $NO_x$ with $NH_3$

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**Abstract:** A $CeO_2/ZrO_2$-$TiO_2$ catalyst was prepared by a stepwise precipitation approach for the selective catalytic reduction of $NO_x$ with $NH_3$. Through the control of pH value and precipitation time during preparation, the function of the $CeO_2/ZrO_2$-$TiO_2$ catalyst could be controlled and the structure with highly dispersed $CeO_2$ (with redox functions) on the surface of the $ZrO_2$-$TiO_2$ (with acidic functions) could be obtained. Characterizations revealed that the obtained $CeO_2/ZrO_2$-$TiO_2$ catalyst could exhibit superior redox functions, outstanding adsorption and activation properties for $NO_x$ and $NH_3$, 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 $NO_x$ with $NH_3$ ($NH_3$-SCR) has been widely applied for the removal of $NO_x$ generated from stationary sources for many years, and it has also become the dominant technology for the control of $NO_x$ emission from diesel vehicles.[1] There have been strong interests in developing vanadium-free catalyst $NH_3$-SCR catalysts with excellent catalytic performance for diesel vehicles.[2-4] In the $NH_3$-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 $NH_3$-SCR catalyst.

## 2. Experimental

The $CeO_2/ZrO_2$-$TiO_2$, 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, $NH_3$, $NO_2$ and $N_2O$, was continuously analyzed by an online FTIR gas analyzer (Nicolet Antaris IGS analyzer). Characterization methods, including XRD, XPS, $H_2$-TPR, $NO_x$-TPD, and $NH_3$-TPD, were used to investigate the catalyst.

## 3. Results and discussion

Due to the strong acidity of the added $Ti(SO_4)_2$ (as the precursor of the Ti), the initial pH of the mixed solution during the preparation of $CeO_2/ZrO_2$-$TiO_2$ 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 $NO_x$ 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.

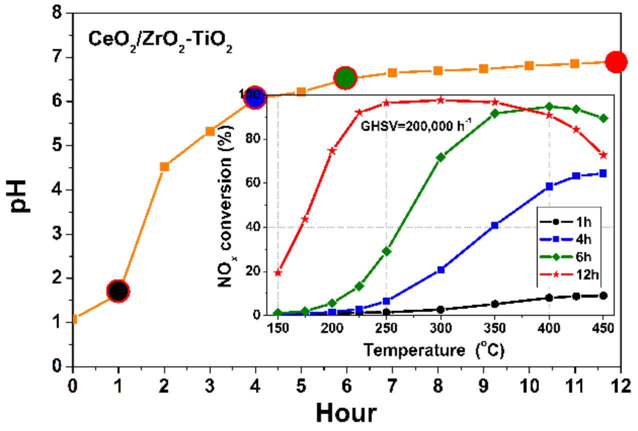

**Figure 1.** The pH variation of the mixed solution during the preparation of the $CeO_2/ZrO_2-TiO_2$ catalysts. $NO_x$ conversions of the obtained samples with different precipitation time were inserted.

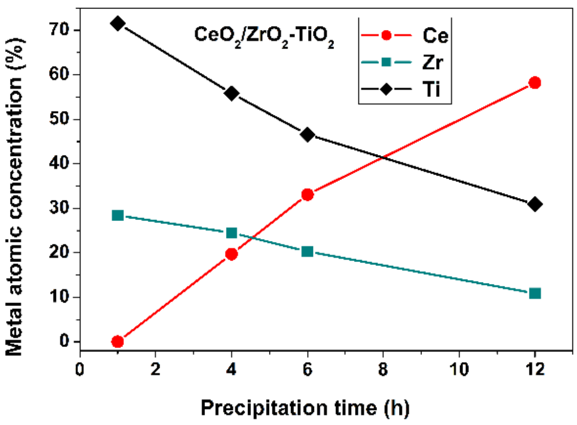

**Figure 2.** Surface metal atomic concentrations of the $CeO_2/ZrO_2-TiO_2$ samples with different precipitation times.

## 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

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