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Full Length Article

# Transition metals (Co, Zr, Ti) modified iron-samarium oxide as efficient catalysts for selective catalytic reduction of $NO_x$ at low-temperature

Ying Wei, Hao Fan, Rui Wang*

*School of Environmental Science and Engineering, Shandong University, Jinan 250199, China*

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ABSTRACT

A series of iron-samarium mixed oxide catalysts modified by zirconium, cobalt and titanium were prepared by co-precipitation method, and the effects of modified transition metal species and calcination temperature in preparation process on $NH_3$-SCR activity were investigated. The catalysts were characterized by TG-DSC, SEM, EDS-mapping, BET, XRD, XPS, PY-IR, $NH_3$-TPD, $O_2$-TPD and in situ DRIFTS. We also investigated the effects of gas hourly space velocity (GHSV), KCl, water vapor and $SO_2$ on $NH_3$-SCR activity over the optimal catalyst. The results indicated that the addition of transition metal could alter the activity of iron-samarium mixed oxide catalyst. In all the samples tested, titanium was illustrated to be the most suitable assistant that could increase surface acid species and acid amount, meanwhile broaden the reaction temperature window and improved the $N_2$ selectivity. Moreover, $Ti_{0.15}Sm_{0.075}Fe_{0.775}O_x$-350 sample possessed best NO conversion rate and excellent resistance to water vapor and $SO_2$. However, The $NH_3$-SCR activity of $K/Ti_{0.15}Sm_{0.075}Fe_{0.775}O_x$-350 was much lower than that of the fresh $Ti_{0.15}Sm_{0.075}Fe_{0.775}O_x$-350. Furthermore, in situ DRIFT study verified the $NH_3$-SCR reaction of $Ti_{0.15}Sm_{0.075}Fe_{0.775}O_x$-350 involved both E–R mechanism and L–H mechanism.

## 1. Introduction

Nitrogen oxides ($NO_x$) are momentous atmospheric pollutants from various emission sources like power plants and motor vehicles. $NO_x$ are bad for environment by the formation of acid rain and photochemical smog. It becomes more and more strict and imminent to control the emission of $NO_x$. So far, selective catalytic reduction of $NO_x$ with ammonia ($NH_3$-SCR) has been considered to be one of the most efficient techniques to improve the conversion of $NO_x$ [1]. The standard SCR reaction is as following:

$$2NH_3 + 2NO + 1/2O_2 \rightarrow 2\,N_2 + 3H_2O$$

while the fast SCR reaction,

$$2NH_3 + NO + NO_2 \rightarrow 2\,N_2 + 3H_2O,$$

also has important effect on the denitrification ($deNO_x$) activity of catalysts. So far, the most commonly used commercial catalyst system is $V_2O_5/TiO_2$ loading with $WO_3$ or $MoO_3$ [2,3] which has high activity in the temperature range of 300–400 °C [4]. Here in, $V_2O_5$ is the contributor of active sites and $WO_3$ is used to increase the activity of catalyst and the stabilization of structure. However, high temperature can bring out the volatilization of vanadium species. Hence, $V_2O_5/TiO_2$ is restricted by its thermal deactivation in high temperature and the toxicity of vanadium [5]. From the above, further development of a high-efficiency and ecofriendly SCR catalyst remains to be a challenge.

Recently, Fe-based catalysts [6,7] have attracted a lot of attention due to their high SCR activity and low toxicity, such as $Fe_{0.2}$-$W_{0.2}$-Ti [8] catalyst exhibited more than 95% $NO_x$ conversion in range of 240–420 °C, and Fe-ZSM-5 [9,10] has also been found to be an effective catalyst. Another star catalyst is the mixture of mental oxides [11,12], for example, $Fe_2O_3$-$WO_3/ZrO_2$ [13] was analyzed systematically where tungsten oxide acted as a bifunctional component to promote the catalytic activity of $Fe_2O_3$ and reduce the susceptibility of thermal aging. However, the temperature window for iron-based catalysts is generally narrow.

On the other hand, large amounts of studies have shown that cobalt can enhance the efficiency of catalysts utilized as auxiliaries [14–16]. Wang et al. [17] studied $CuCo/CeO_2$ which showed activity at a wide temperature range, and the $NO_x$ conversion rate was more than 80% at 200 °C. What is more, Liu et al. [18] proved that cobalt could increase the strong acid sites on the catalyst. As a promoter, $ZrO_2$ is often used to optimize catalytic activity as well, due to its amphoteric property and strong ability of ion migration [5]. Jiang et al. [19] found Zr modified Fe – Mn/Ti catalyst could increase the NO conversion rate below 150 °C and alleviated the $SO_2$ poisoning. Besides, $TiO_2$ with high specific

* Corresponding author.
*E-mail address:* wangrui@sdu.edu.cn (R. Wang).

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surface area and favorable adsorption capability of $NH_3$ and $SO_2$ is often used as carrier or agent of $NH_3$-SCR catalyst too [20–25].

In previous works, rare earth samarium has been introduced to improve the activity of catalyst in the low temperature [26–28], Sun et al. [29] demonstrated that the addition of Sm could effectively enhance the low-temperature SCR activity and $SO_2/H_2O$ resistance of $Ce/TiO_2$ catalyst. On the other hand, we also have found that the addition of samarium could increase the $NH_3$-SCR activity based on iron oxide catalyst in our previous research, however, its active temperature window was narrow. Therefore, we need to further optimize iron-samarium mixed oxide catalyst.

In the present work, iron-samarium mixed oxide catalyst was modified respectively by zirconium, cobalt and titanium with co-precipitation method. The effects of transition metal species, content of optimal transition metal and calcination temperature in preparation process were investigated. The best one was selected to investigate the influence of GHSV, poisoning caused by potassium and $SO_2$. And physicochemical properties of samples were characterized by TG-DSC, SEM, EDS-mapping, BET, XRD, XPS, PY-IR and $NH_3$-TPD.

## 2. Materials and method

### 2.1. Materials and reagents

In this work, all reagents and solvents used were A.R. grade, without further purification. $Sm(NO_3)_3{\cdot}6H_2O$ was purchased from Minmetals rare earth research institute (Beijing) Co. Ltd. $Fe(NO_3)_3{\cdot}9H_2O$ and $Co(NO_3)_2{\cdot}6H_2O$ were received from the Kermel Reagent Co. Ltd. $NH_3{\cdot}H_2O$ was supplied by Laiyang Kangde Chemical Co. Ltd. KCl was produced by Tianjin Fu Chen Fine Chemical Co. Ltd. $ZrOCl_2{\cdot}8H_2O$ and $Ti(SO_4)_2$ were purchased from the National Drug and Chemical Group Co. Ltd.

### 2.2. Catalysts preparation

A series of modified iron-samarium mixed oxide catalysts were prepared by co-precipitation. In typical process, firstly, $Fe(NO_3)_3{\cdot}9H_2O$, $Sm(NO_3)_3{\cdot}6H_2O$ and $Co(NO_3)_2{\cdot}6H_2O$ (or $ZrOCl_2{\cdot}8H_2O$, $Ti(SO_4)_2$) were dissolved in deionized water to obtain a mixture solution, with the total ion concentration was 0.2 mol/L, and then the pH value of the solution was adjusted to 8.5–10 using dilute aqueous ammonia under vigorous mixing. After the slurry was filtered by vacuum filtration, the obtained solid was washed by deionized water several times to remove anion impurities. After dried at 105 °C for 12 h and then calcined at a certain temperature for 5 h (heating rate was kept at 5 °C $min^{-1}$), the final product was marked as $L_ySm_{0.075}Fe_{0.925-y}O_x$-T (L = Co, Zr, Ti), where y represented the molar ratio of L/(L + Sm + Fe) in catalyst, x represented the mole number of oxygen in catalyst, and T indicated the calcination temperature. Finally, the obtained sample was crushed and sieved to 40–60 mesh for test.

In the simulation of potassium salt poisoning experiment, KCl was loaded on $Ti_{0.15}Sm_{0.075}Fe_{0.775}O_x$-350 by incipient impregnation method. Deionized water was used as impregnating solvent, and the mass fraction of loading KCl was 8%. Finally, catalyst obtained was marked as $K/Ti_{0.15}Sm_{0.075}Fe_{0.925-y}O_x$-350.

### 2.3. Catalyst characterization

Thermogravimetric (TG) and differential scanning calorimetry (DSC) analysis of obtained samples were carried out with SDT Q600 Universal V4.1D TA instrument under a flow of $N_2$ from 100 °C to 700 °C at a heating rate of 10 °C·$min^{-1}$. Field emission scanning electron microscopy (FESEM) and energy dispersive spectrometer mapping (EDS-mapping) were conducted by ZeissSupra 55. Powder X-ray diffraction (XRD) measurement was used to verify the crystallographic phases in $L_ySm_{0.075}Fe_{0.925-y}O_x$-T. The XRD patterns of samples were conducted with Bruker D8 Advanced diffractometer with Cu target Kα-ray, and Nickel filter was utilized to ensure the incoming x-rays were monochromatic. In addition, the scanning angle was from 10 to 70° of 2θ at a scanning rate of 2° per minute. Pyridine Adsorption Fourier-transform Infrared (Py-IR) was obtained by PE Frontier FT-IR Spectrometer. The X-ray photoelectron spectroscopy (XPS) analyses of samples were performed with Thermo Fisher Scientific ESCALAB 250 spectrometer to investigate the chemical states of atoms at catalyst surface. $NH_3$-TPD and $O_2$-TPD were finished by thermal conductivity detector (TCD) with the heating rate was kept at 8 °C·$min^{-1}$. BET Surface areas of samples were measured by Micromeritics TriStarII 3020 Surface Area and Porosity Analyzer (at 77 K, $N_2$ as the adsorbent). Prior to $N_2$ physisorption, the catalysts were degassed at 150 °C for 2 h. The specific surface areas were calculated by multi-point Brunauer-Emmett-Teller (BET) approach. The $N_2O$ concentration was measured by Agilent 7890B, and the $N_2$ selectivity was calculated by $[N_2]/([N_2] + [N_2O])$.

In situ DRIFTS spectra were recorded using Thermofisher Nicolet iS 50. Before the adsorption experiment of $NH_3/NO + O_2$, the catalyst was heated to 250 °C (heating rate was kept at 5 °C·$min^{-1}$) under $N_2$ at a total flow rate of 100 ml·$min^{-1}$ for 1 h to remove adsorbed impurities. A background spectrum was collected under flowing $N_2$ and was subtracted from the sample spectra. The adsorption experiment of $NH_3/NO + O_2$ lasted for 60 min, subsequently purged with $N_2$ for 30 min, and then the feed gas was changed to $NO + O_2/NH_3$ respectively in the transient studies. The DRIFTS spectra were recorded by accumulating 100 scans with a resolution of 4 $cm^{-1}$.

### 2.4. $NH_3$-SCR activity

The $NH_3$-SCR activity experiments were carried out in a fixed bed reactor placed in the center of a tubular furnace. The concentration of NO was measured by TH-990S NO flue gas analyzer (Wuhan Tianhong instrument Co. Ltd.). In the $NH_3$-SCR reaction, the catalyst was positioned in the quartz tube whose inner diameter was 8 mm between two layers of quartz wool. The typical reaction condition was regulated by mass controllers as following: 600 parts per million by volume (ppmv) NO, 650 ppmv $NH_3$, 6% $O_2$ and $N_2$ was the equilibrium gas. In typical experiment, 0.38 g sample was used in each run. The total flow rate was 100 ml·$min^{-1}$ corresponding to a gas hourly space velocity (GHSV) of 15000 $h^{-1}$. The NO conversion rate was expressed as $(C_0 - C)/C_0 \times 100\%$, where $C_0$ standed for the concentration of NO in the feed gas and C standed for the concentration of NO in the outlet gas.

## 3. Results and discussion

### 3.1. Effects of modified transition metal species

#### 3.1.1. SCR catalytic activity

Fig. 1 shows the de-$NO_x$ activities of $Sm_{0.075}Fe_{0.925}O_x$-400 and catalysts modified by Zr, Co, Ti. It can be obviously found that all the obtained samples showed high catalytic activity among 200–250 °C. Furthermore, when the reaction temperature was below 200 °C, $Ti_{0.1}Sm_{0.075}Fe_{0.825}O_x$-400 sample possessed the best activity up to 95% at 150 °C, and the SCR activity of $Sm_{0.075}Fe_{0.925}O_x$-400 sample was obviously enhanced by the addition of modified transition metal species when temperature was above 250 °C. In addition, as shown in Fig. 2(a), the $N_2$ selectivity of $Ti_{0.1}Sm_{0.075}Fe_{0.825}O_x$-400 and $Zr_{0.1}Sm_{0.075}Fe_{0.825}O_x$-400 was above 95% which was higher than that of $Sm_{0.075}Fe_{0.925}O_x$-400 between 100 and 250 °C, proving those two modified samples had excellent $N_2$ selectivity. Moreover, the $N_2O$ concentration of outlet gas using $Co_{0.1}Sm_{0.075}Fe_{0.825}O_x$-400 as catalyst was much higher than others between 150 and 250 °C, as shown in Fig. 2(b). Based on the above results, titanium was eventually verified to be the optimal one. The addition of titanium could overall improve the SCR activity and $N_2$ selectivity, moreover, widen the reaction temperature window at the same time.