



Investigating the role of $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ in the acidity, oxidability and activity of $\text{H}_4\text{SiW}_{12}\text{O}_{40}\text{-Fe}_2\text{O}_3$ catalysts for the selective catalytic reduction of NO with NH_3



Dong Ye, Ruiyang Qu, Yongxin Zhang, Weihong Wu, Shaojun Liu, Chenghang Zheng, Xiang Gao*

State Key Laboratory of Clean Energy Utilization, Department of Energy Engineering, Zhejiang University, Hangzhou, 310027, China

ARTICLE INFO

Keywords:

$\text{H}_4\text{SiW}_{12}\text{O}_{40}$
 Fe_2O_3
 Acid properties
 Redox properties
 Activity

ABSTRACT

A series of $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ -modified Fe_2O_3 catalysts were synthesized using the precipitation method. Over 80% NO_x conversion was obtained in the temperature region of 250–450 °C for the catalysts with the $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ content of 5% and 10%. The relationship between the physicochemical properties and performances of the series catalysts was established. Abundant acid sites were introduced with doping $\text{H}_4\text{SiW}_{12}\text{O}_{40}$, which promoted the adsorption of reductant NH_3 on the catalysts at high-temperature regions. Moreover, adding $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ lowered the amount and reducibility of catalyst surface reactive oxygen species, which inhibited the oxidation of NH_3 to NO_x at higher temperatures to some extent. Thus, most ammonia species were prone to participating in the reaction with NO_x instead of being directly oxidized to NO_x in the higher temperature region over the $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ -decorated catalysts. And it could be concluded that the balance of the acid and redox properties constituted the main reason for the superior activity of the high $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ content catalysts. Additionally, SO_2 exerted a slight and reversible inhibition effect on the catalyst activity at 300 °C, suggesting that HSiW-modified Fe_2O_3 oxide might be a promising catalyst in practical applications.

1. Introduction

The selective catalytic reduction of NO with NH_3 (SCR) is confirmed to be an effective technology for the abatement of NO_x from both mobile and stationary sources [1]. WO_3 or MoO_3 promoted $\text{V}_2\text{O}_5/\text{TiO}_2$ is the commercialized catalyst system in stationary applications. However, several actual problems come out in the applications of this catalyst system, such as the narrow operation temperature window (320–420 °C), and the toxicity of vanadium species to environment and human health. For these reasons, much attention has been focused on the development of efficient and environmentally benign catalysts, aiming to replace the present V_2O_5 -based catalyst system.

It is well-accepted that the coexistence of acid and redox functions can be detected in the SCR catalysts [1]. The enhanced redox properties are considered to promote the activation of the adsorbed ammonia species and NO_x , which mainly explains the high reactivity of catalysts in the lower temperature region [2,3]. However, a decline in the deNO_x efficiency is always observed at a temperature higher than 400 °C for the catalysts possessing an excellent low-temperature activity [4]. It seems that a strong catalyst oxidability exerts a negative effect on the high-temperature SCR reactions. By contrast, the addition of SO_2 makes

the catalyst operation temperature window shift towards higher temperatures in a certain extent; the enhanced acid properties, together with the weakened redox properties resulting from the formation of sulfated active components might explain the declined low-temperature activity of the catalysts and the promoted SCR reactions at high-temperature regions to some extent [5,6]. It seems that the balance of the acid and redox properties could make a catalyst possess an excellent activity in a wide temperature range, on which scanty research has been conducted. But knowledge of such effects might help to get insight into the correlations between the physicochemical properties and performances of the catalysts and provide a theoretical basis for the design of new catalyst systems.

Fe_2O_3 is widely used as catalyst support, promoters and active components in the SCR reactions [7,8]; the novel reducibility and a lack of surface acid sites illustrate that Fe_2O_3 could mainly provide redox sites for the activation of NH_3 and NO_x [2]. $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ (HSiW for short) is well-known for its extraordinarily strong acidity, on which abundant acid sites could be available for the adsorption of NH_3 [9]. Therefore, a combination of Fe_2O_3 which possesses an excellent redox behavior and HSiW with a unique acid property might help to investigate the effect of acidity and oxidability on the SCR activity of the

* Corresponding author.

E-mail address: xgao1@zju.edu.cn (X. Gao).

catalysts. And a satisfactory activity and N₂ selectivity might be obtained through tuning the loading amount of HSiW.

For these reasons, a series of HSiW-modified Fe₂O₃ catalysts were prepared in this study. The relationship between the physicochemical properties and performances of the catalysts would be explored, which aims to discover the importance of the balance of the catalyst acid and redox properties in the SCR reactions. X-ray diffraction (XRD), N₂ adsorption and Raman spectra were conducted to investigate the physical structures of the series catalysts. NH₃ temperature-programmed desorption (NH₃-TPD) and *in situ* diffuse reflectance Fourier transform spectroscopy (*in situ* DRIFTS) were carried out to discover the role of HSiW in the acidity of the catalysts. H₂ temperature-programmed reduction (H₂-TPD) and X-ray photoelectron spectroscopy (XPS) were adopted to study the variations in the catalyst redox properties through adding HSiW. Finally, SO₂ tolerance tests were carried out to illustrate that HSiW-modified Fe₂O₃ oxide might be a promising catalyst in practical applications.

2. Experimental

2.1. Chemicals

P25 (85%: anatase, 15%: rutile; S_{BET} = 55 m²g⁻¹) was purchased from Degussa. NH₄VO₃ (AR: 99.0%), H₄₀N₁₀O₄₁W₁₂xH₂O (AR, WO₃ content: 85%–90%), H₄SiW₁₂O₄₀xH₂O (AR), ammonium hydroxide (AR: 25%–28%), C₂H₂O₄·2H₂O (AR: 99.5%) and Fe(NO₃)₃·9H₂O (AR: 98.5%) were available from Sinopharm Chemical Reagent Co., Ltd. N₂, O₂, NO (0.5% NO + 99.5% N₂), SO₂ (0.5% SO₂ + 99.5% N₂), and NH₃ (0.5% NH₃ + 99.5% N₂) were obtained from Hangzhou New Century Mixed Gas Co., Ltd.

2.2. Preparation of the samples

Fe₂O₃ support (named as Fe) was prepared using the precipitation method. The calculated amount of Fe(NO₃)₃ was dissolved in deionized water. The obtained solution was slowly added into the excess ammonia solution under continuous stirring. After that, the precipitates were obtained by filtration, washed by deionized water for several times, dried at 110 °C for 8 h and then calcined at 500 °C in air for 5 h.

As for the preparation of the HSiW-modified catalysts, the as-prepared Fe₂O₃ support was immersed into HSiW solution. Excess water was removed by using a rotatory evaporator. The HSiW loading amount was determined by tuning the concentration of the used solution. All the catalysts were dried at 110 °C overnight and then calcined at 500 °C for 5 h. Finally, the obtained catalysts were crushed and sieved into 40–60 meshes for the activity tests. The samples were named based on the content of HSiW. For example, 10% HSiW-Fe means that 10 wt.% HSiW was loaded on the Fe surface.

V₂O₅-WO₃/TiO₂ catalyst (donated as VW/Ti) containing 1 wt.% V₂O₅ and 5 wt.% WO₃ was synthesized using the wet-impregnation method. Certain amounts of NH₄VO₃ and H₄₀N₁₀O₄₁W₁₂xH₂O were dissolved in oxalic solution. And then 4 g P25 was immersed into the obtained solution. The mixture was stirred for 2 h, dried at 110 °C in air overnight and calcined at 500 °C for 5 h. Finally, the catalyst was crushed and sieved into 40–60 meshes for the activity tests.

2.3. Reaction systems

Activity tests of the series catalysts were conducted in the reaction system. 0.2 g catalyst was used for evaluation. The reactant gases contained 500 ppm NO, 500 ppm NH₃, 5% O₂ and N₂ in balance. The total gas flow rate was 500 mL min⁻¹, related to a gas hourly space velocity (GHSV) of 150,000 mLg⁻¹h⁻¹. The concentrations of NO, NO₂, N₂O and NH₃ were recorded on a Nicolet iS50 FTIR spectrometer. The NO_x conversion (X), N₂ selectivity (S) and NH₃ conversion (N) could be calculated using the following equations:

$$X = 100\% \times ([NO_{in}] - [NO_{out}] - [NO_{2out}])/[NO_{in}] \quad (1)$$

$$S = 100\% \times [1 - (2 \times [N_2O_{out}] + [NO_{2out}])]/([NO_{in}] + [NH_{3in}]) \quad (2)$$

$$N = 100\% \times ([NH_{3in}] - [NH_{3out}])/[NH_{3in}] \quad (3)$$

NH₃ oxidation experiments were performed in the reaction system. A sample of 0.2 g was used. The reaction conditions were as follows: 500 ppm NH₃, 5% O₂ and N₂ balanced gas. The GHSV was 150,000 mLg⁻¹h⁻¹. The compositions of the tested gases were analyzed using a Nicolet iS50 FTIR spectrometer. The NH₃ conversion (N) could be calculated based on Eq. (3).

Catalyst sulfur resistance tests were carried out in the reaction system. The compositions of the reactant gases were as follows: 500 ppm NO, 500 ppm NH₃, 500 ppm SO₂, 5% O₂ and balanced N₂ at a flow rate of 1.2 L min⁻¹. The GHSV was 240,000 mLg⁻¹h⁻¹. The NO_x conversion of the catalysts at certain time could be calculated according to Eq. (1).

2.4. Characterization of the samples

XRD measurements were conducted on a Rigaku D/max 2550PC system using the CuKα radian source. Raman spectra of the series samples were recorded using a Renishaw inVia spectrometer with an Ar ion laser as the radian source under ambient conditions.

N₂ adsorption and desorption experiments were performed to study the textural properties of the series catalysts. The Brunauer-Emmett-Teller (BET) method was adopted to calculate the catalyst specific surface areas. Catalyst pore size distributions were determined using the Barrett-Joyner-Halenda (BJH) method.

XPS experiments were performed on an ESCALab220i-XL electron spectrometer using Al Kα radian. The binding energies of the series photoelectron peaks were calibrated using the C 1s line at 284.5 eV.

NH₃-TPD experiments were carried out on an automated catalyst characterization system (Micromeritics, model AutoChem II 2920). Each sample of 0.1 g was first pretreated at 300 °C in flowing Ar for 30 min. And then the tested sample was cooled to 60 °C and saturated with NH₃ for 1 h. After that, the sample was flushed by Ar for 2 h to remove the physically adsorbed NH₃. Finally, the sample was heated to 600 °C in Ar at a heating rate of 10 °C min⁻¹. NH₃ signal was recorded using a mass spectrometer.

H₂-TPR profiles of the series catalysts were obtained on an automated catalyst characterization system (Micromeritics, model AutoChem II 2920). A sample of 50 mg was first pretreated under Ar atmosphere at 350 °C for 30 min. After that, the tested sample was cooled to 60 °C and then heated to 800 °C in H₂ with a ramping rate of 10 °C min⁻¹. The consumption of H₂ was monitored using a thermal conductivity detector (TCD).

In situ DRIFTS experiments were carried out on an FTIR spectrometer (Nicolet 6700). Each sample was first pretreated at 350 °C in N₂ for 1 h to remove the adsorbed impurities. The background spectra were collected at certain temperatures (100 °C, 150 °C, 200 °C, 250 °C, 300 °C, 350 °C) in flowing N₂. After that, 1000 ppm NH₃ was purged into the cell and the sample was saturated with NH₃ at 100 °C for 1 h. And then the sample was flushed by N₂ to remove the physically adsorbed NH₃. Finally, the sample was heated to certain temperatures in N₂ to detect the variations in the surface NH₃ species. All the spectra were obtained at a resolution of 4 cm⁻¹ typically averaging 64 scans.

3. Results and discussions

3.1. Catalyst performances

3.1.1. SCR activity

The activity of the series catalysts in the temperature region of 150–450 °C was illustrated in Fig. 1(a). Pure Fe support exhibits a poor activity. The NO_x conversion of pure Fe support shows a slight upward

Download English Version:

<https://daneshyari.com/en/article/8916908>

Download Persian Version:

<https://daneshyari.com/article/8916908>

[Daneshyari.com](https://daneshyari.com)