Applied Surface Science 459 (2018) 639–646

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Full Length Article

The effects of tungsten and hydrothermal aging in promoting NH_3-SCR activity on V_2O_5/WO_3-TiO_2 catalysts

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ARTICLE INFO

Keywords:
V_2O_5/WO_3-TiO_2
Hydrothermal treatment
Polymeric surface VO_x
Low valence vanadium
NH_3-SCR

ABSTRACT

The fresh catalysts of V_2O_5-TiO_2 (VTi) and V_2O_5/WO_3-TiO_2 (VWTi) were prepared *via* an impregnation method. The hydrothermal aged samples were obtained at 750 °C for 24 h under airflow with 10 vol% water vapor. Compared to the fresh catalysts, the catalytic performance of the aged catalysts (VTi-A and VWTi-A) has been significantly improved. Particularly, VWTi-A displayed the best activity over a wide temperature range (NO_x conversion: > 90% @ 250–550 °C). Structural characterizations indicated that the surface area of the aged catalysts was dramatically decreased, and the morphologies of catalysts also changed. The X-ray photoelectron spectroscopy (XPS), H_2 temperature-programmed reduction (H_2-TPR), and Raman results demonstrated that hydrothermal aging greatly influenced the migration and agglomeration of vanadium species. As a result, numerous active polymeric VO_x species were emerged on the surface of catalysts. More importantly, XPS results revealed that more low valence vanadium species (V^{4+} and V^{3+}) was produced on the VWTi-A catalysts than that of VTi-A after hydrothermal aging. These low valence vanadium species resulted in considerably higher SCR activity than the high valence vanadium species (V^{5+}). Consequently, both polymeric surface VO_x species and low valence vanadium species determined the enhanced low-temperature SCR behavior of the aged catalysts.

1. Introduction

Due to the higher activity and better SO_2 resistance, V_2O_5-TiO_2 as SCR catalysts have been widely used in stationary sources for many decades [1,2]. And it is also considered as an efficient catalyst to remove the NO_x emitted from diesel engines, which is received much attention because of the increasingly stringent regulations [3,4]. However, it is limited by the thermal deactivation of the catalysts in high temperature exhaust gas (reach 750 °C). The deactivation is mainly due to the phase transition of TiO_2 from anatase to rutile, and segregation or volatilization of vanadia species at the severely temperature [5,6].

Many efforts have been made to improve the thermal stability of V_2O_5-TiO_2 based catalysts. One approach is to use metal vanadates as active sites to suppress the deactivation pathway, such as rare earth vanadates [3,7–10] and $FeVO_4$ [11,12]. Another way is to modify the catalyst by introducing heterogeneous components such as alumina, silica, zirconia [13–16]. Among these introduced components, tungsten is an ideal promoter, which is widely investigated many years. Several studies reveal that tungsten can inhabit the phase transition of TiO_2, increase the acidity and improve the SO_2 resistance [17–19]. Therefore, V_2O_5/WO_3-TiO_2 is the main choice for the commercial catalyst used in the SCR.

Interestingly, relevant experimental evidences demonstrate the tungsten not only improves the thermal stability of V_2O_5/WO_3-TiO_2 catalyst, the SCR activity is also enhanced after the treatment of severely temperature. Madia et al. reported the SCR activity of V_2O_5/WO_3-TiO_2 catalysts increased after thermal aging with 1 or 2% V_2O_5 loading [8]. Hagi et al. found the addition of WO_3 enhanced the SCR performance and obtained the maximum upon calcination at 823 K [20]. And Nova et al. proved the SCR activity increased after calcination at 1073 K along with the decreased N_2 selectivity in the V_2O_5/WO_3-TiO_2 catalysts [5]. The above observations show a new understanding of the function of tungsten on the V_2O_5/WO_3-TiO_2 catalysts under the severely conditions. However, the natures are still under debate and meaningful to investigate.

In the present study, the addition of tungsten and a hydrothermal treatment were applied to generate different distributions of VO_x

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https://doi.org/10.1016/j.apsusc.2018.08.046
Received 13 March 2018; Received in revised form 13 June 2018; Accepted 5 August 2018

species on TiO_2 support. Various techniques (i.e., X-ray photoelectron spectroscopy, X-ray diffraction, H_2 temperature programmed reduction, Transmission electron microscope and Raman spectra) were employed to probe the location and state of VO_x species before and after hydrothermal aging. The evolution of VO_x species was examined, and the relevant mechanism was investigated systematically.

2. Experimental

2.1. Catalyst preparation

The WO_3-TiO_2 was synthesized by mixing metatitanic acid (H_4TiO_4) and ammonium paratungstate ($(NH_4)_6H_2W_{12}O_{40}\cdot xH_2O$) with the weight ratio of WO_3:TiO_2 = 5:95. The obtained suspension was stirred for 1 h and titrated by 25 wt% ammonium hydroxide ($NH_3\cdot H_2O$) until pH = 9. The precipitate was stirred for 2 h, dried at 100 °C over night and calcined at 550 °C for 4 h in the muffle. The pristine TiO_2 was prepared by the same process without adding ammonium paratungstate.

V_2O_5/TiO_2 and V_2O_5/WO_3-TiO_2 samples with 1 wt% V_2O_5 were prepared as follows. 0.13 g ammonium metavanadate (NH_4VO_3) was dissolved into a mixed solution composed of 3 ml monoethanolamine (C_2H_7NO) and 5 ml deionized water. The obtained solution was added into 20 ml suspension contained 20 g supporter (TiO_2 and WO_3-TiO_2). The subsequent drying and calcination conditions were consistent with the preparation of the WO_3-TiO_2. And the resultant catalysts were named as VTi and VWTi.

Finally, a hydrothermal treatment was performed at 750 °C for 24 h under a flowing air atmosphere with 10 vol% water vapor to obtain the aged samples, which were denoted as VTi-A and VWTi-A.

2.2. Catalyst characterizations

X-ray diffraction (XRD) was performed on Shimadzu X-ray diffractometer 6100 (Cu Kα radiation, $\lambda = 1.5418$ Å) with $2\theta = 10°–90°$. The specific surface areas and pore size distributions were determined by N_2 adsorption/desorption isotherms at 77 K with Brunanuer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods (TriStar II 3020 analyzer, Micromeritics, USA). Raman spectra were recorded on a Raman spectrometer (Invia, Renishaw) with an argon laser as the excitation source operating 532 nm under atmospheric pressure. The morphology and microstructure were observed using transmission electron microscopy (TEM, FEI, Tecnai G2 F30). The surface oxidation states of samples were determined by X-ray photoelectron spectroscopy (XPS, Thermo Fisher ESCALAB 250Xi analyzer). The binding energies (BE) of various elements were calibrated using C 1s peak (284.6 eV). H_2-TPR and O_2-TPD experiments were conducted on TP-5080 automated chemisorptions analyzer (Xianquan, China). 50 mg sample was pretreated in a flow of N_2 (30 ml min^{-1}) at 250 °C for 20 min and then cooled to room temperature. After stabilization, TPR experiments were performed from 100 to 800 °C at 10 °C min^{-1}. O_2-TPD experiments were carried out as follows. 100 mg sample was pretreated in a flowing He (30 ml min^{-1}) at 500 °C for 30 min and then cooled to room temperature. After O_2 saturation in 1 h, the gas was switched to He for 0.5 h. Then TPD was performed by ramping the temperature at 10 °C min^{-1} to 900 °C.

2.3. Catalytic activity tests

NH_3-SCR activity measurements were carried out in a fixed-bed quartz reactor with 0.8 ml catalysts (pressed, crushed and sieved to 50–80 mesh) from 175 to 550 °C under atmospheric pressure. The reactant gas mixture consisted of 500 ppm NO, 500 ppm NH_3, 5% O_2, 10% H_2O and N_2 as balance gas with GHSV of 50000 h^{-1}. Before testing, the catalyst was pretreated with 5% O_2/N_2 at 500 °C for 30 min. The outlet gas was monitored by a flue gas analyzer (ECOM EN-2F, RBR, Germany). The NO_x conversion was calculated according to Eq. (1) below:

$$NO_x\text{conversion}(\%) = \frac{[NO]_{in} - [NO]_{out} - [NO_2]_{out}}{[NO]_{in}} \times 100 \tag{1}$$

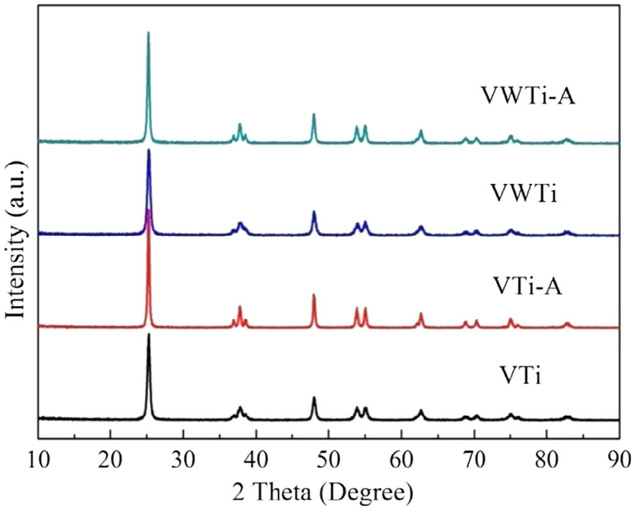

Fig. 1. XRD patterns of VTi, VTi-A, VWTi and VWTi-A catalysts.

3. Results and discussion

3.1. Textural and microstructural characterizations

Fig. 1 shows the XRD patterns of the prepared catalysts. For all the samples, the diffraction peaks can be indexed to the typical anatase TiO_2 (PDF#44-0477). No diffraction peaks of WO_3, V_2O_5 or rutile TiO_2 are detected, even after hydrothermal aging. This result implies that the catalysts are very stable, or the contents of the formed oxides are too low to be detected [21–23]. However, the peaks of the aged catalysts become sharper, and their intensities are much higher than the fresh ones. Moreover, the crystallite sizes are calculated by Scherer equation on the basis of the peak width of (1 0 1) plane, as summarized in Table 1. After hydrothermal aging, the crystallite sizes of VTi-A and VWTi-A are increasing from 20.6/17.7 nm to 30.3/26.4 nm, respectively. Obviously, the addition of tungsten could inhibit the grain growth during hydrothermal aging.

The N_2 adsorption-desorption isotherms and pore size distributions of the catalysts are exhibited in Fig. 2. As shown in Fig. 2a, all the samples show the typical IV isotherms with H3 hysteresis loops, exhibiting the mesopores feature derived from the packing of nanoparticles [24,25]. Fig. 2b shows the pore size distributions of four catalysts. It reveals that the pore diameters of VTi-A and VWTi-A are greatly larger than that of VTi and VWTi. As shown in Table 1, the surface area and micropore volume are decreased after hydrothermal aging, whereas the pore diameters increase. Moreover, these changes in VWTi are less than that of VTi, indicating that the existence of tungsten

Table 1
Crystallite sizes, particle sizes and textural properties of the catalysts.

Catalysts	Crystallite size (nm)[a]	Particle size (nm)[b]	Surface area ($m^2\,g^{-1}$)	Pore volume ($cm^3\,g^{-1}$)	Average pore diameter (nm)
VTi	20.6	21.2	59.28	0.34	21.2
VTi-A	30.3	31.6	26.51	0.24	43.8
VWTi	17.7	18.3	65.50	0.33	17.6
VWTi-A	26.4	28.1	36.66	0.24	26.8

[a] Calculated by the Scherer formula on basis of XRD results.
[b] Measured from TEM images.