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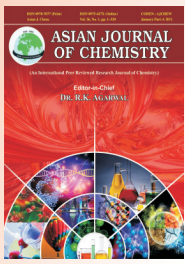

Behaviours of V_2O_5-WO_3-TiO_2 SCR Catalyst after Thermal Aging

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The influence of thermal aging on catalytic activity, weight loss, phase structure, surface area and pore characteristic of commercial V_2O_5-WO_3-TiO_2 selective catalytic reduction (SCR) catalyst were investigated using a fixed bed reactor, TG-DTA, XRD and nitrogen adsorption. The catalyst showed good catalytic activity and thermal stability in fresh state or aging for 50 h at 550 °C and 650 °C in air. The catalyst drastically deactivation after calcination for 50 h at 650 °C in air, the maximum conversion of NO dramatically decreased from 100 to 60 %, the light off temperature increased from 187 to 360 °C. The analysis revealed that the deactivation of catalyst was caused by three factors. Firstly, the reduction of vanadia loading was caused by the vocalization; secondly, the reduction of the active site was resulted from the interaction V_2O_5 with TiO_2 and lastly, the changes of reaction area and pore structure were due to the phase transformation of TiO_2 from anatase to rutile.

Keywords: V_2O_5, WO_3, TiO_2, Catalyst, Thermal, Aging.

INTRODUCTION

The V_2O_5-WO_3-TiO_2 catalyst having high catalytic activity has been widely used for selective catalytic reduction (SCR) of NO_x form the exhaust gas of heavy duty and stationary factory in Europe, USA, *etc.*[1-3]. China is implementing the stages-IV emission standard for heavy duty from July 1, 2013. The V_2O_5-WO_3-TiO_2 catalyst has developed the only after treatment technology for purify NO_x in order to achieve stages-IV emission standard of heavy duty in China due to excellent catalytic activity and good sulfur tolerance. The one of the biggest challenges of catalyst is durability in application. Numerous studies have been conducted regarding the deactivation of V_2O_5-WO_3-TiO_2 SCR catalyst which was applied in stationary sources. These studies focused on the chemical deactivation by alkaline, alkaline earth metals, transition metals, additives, impurity of fuels, *etc*[4-8]. These authors suggested that strong deactivation of catalyst due to a reduced ammonia storage capacity by alkaline and alkaline earth metals, which occupy the non-atomic hole sites of the (010) V_2O_5 surface and block both of the Brønsted acid and V^{5+} = O sites. Phosphate is a strong deactivating component, which results in loss of catalyst surface area due to surface masking, pore blocking and condensation[9].

Actually, the main problem is the thermal deactivation for V_2O_5-WO_3-TiO_2 SCR catalyst used in heavy duty. The reported literature usually studied the influence of component on the thermal stability of V_2O_5-WO_3-TiO_2 SCR catalyst[10-13]. Studies show that the addition of tungsten and silica can improve the thermal properties of catalyst. The activity of catalyst including barium drastically decreased after aging for 6 h at 600 °C due to the interaction V_2O_5 and BaO at high temperature. It is noted that the vanadium content has a major influence on the SCR activity and thermal ability. Catalyst containing higher vanadium content showed a better SCR activity. Conversely, higher vanadium content resulted in lower thermal durability. The catalyst containing 2 % V_2O_5 represented an optimal compromise between high SCR activity and good thermal stability. Casanova *et al.*[14] investigated the influence of rare-earths on the thermal stability of SCR catalyst. The results show that La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Er and Yb has a significant improvement in thermal stability, especially, Tb has the best effect.

In the present study, we investigated the behaviors of V_2O_5-WO_3-TiO_2 SCR catalysts after aging for different conditions. The catalytic activity was evaluated by testing the light off temperature and calculating NO conversion in a fix bed reactor, the weight loss of catalyst materials was tested by TG method.

The phase structure, pore structure and surface area were investigated by XRD and nitrogen adsorption method.

EXPERIMENTAL

Catalyst preparation and reaction system: The V_2O_5-WO_3-TiO_2 catalyst is commercial product in China. It is prepared by two-steps method. The first step for the synthesis of the V_2O_5-WO_3-TiO_2 catalytic material, the second step for the preparation of catalyst samples by coating the cordierite honeycomb substrate with V-W-TiO_2 slurry, followed by dryness and calcinations. To investigate the behaviors of catalysts under different aging conditions, there are threes kind of catalysts as follow: SCR-F: fresh catalyst. SCR-A1: The catalyst was left for 200 h at 550 °C. SCR-A2: The catalyst was left for 200 h at 650 °C.

Evaluation of catalytic activity: The catalytic activity of SCR catalysts were carried out by a fixed bed flow reactor system with a quartz reactor in which the catalyst samples with a diameter 16 mm and length 40 mm were fixed.

The NO conversion of catalyst was determined under steady state conditions at Space velocities of 20000 h^{-1} and at temperature varying between 150 °C and 450 °C. The composition of the reactor feed is 300 ppm NO, 300 ppm NH_3, 10 % O2, 7 % H_2O, 8% CO_2 and balance N_2. The concentration of outlet gas was analyzed by FT-IR.

Characterization: The weight loss of materials were measured by TG-DTA method with NETZSCH STA 409 PC/PG apparatus using gas air at the heating rate of 10 K/min and at temperature varying between room temperature and 1133 °C.

The Phase structures of materials were measured by using a Rigaku D/MAX-RC X-ray diffractometer. Ni-filtered Cu-K_α radiation was used as an X-ray gun operated at 40 kV and 100 mA. Diffraction patterns were obtained at the scanning rate of 10 °/min.

The pore structures of materials were measured by using Quantachrome NovaWin2 sorption analyzer. The powder were pretreatment at 150 °C for 15 min in vacuum before the adsorption testing. The surface area and pore volume were calculated by DFT method.

RESULTS AND DISCUSSION

Catalytic activity: The NO conversion of SCR-F, SCR-A1 and SCR-A2 catalyst is given in Fig. 1. The figure shows the fresh catalyst has good SCR activity. The light-off temperature is 187 °C and the NO conversion is 100 % in high temperature. The NO conversion didn't loss compare with the fresh catalyst after aging for 200 h at 550 °C. The curve of NO conversion of SCR-A1 is accord with the SCR-F1, which denote that the V_2O_5-WO_3-TiO_2 catalysts does not appear deactivation and keep good durability at 550 °C. The SCR-A2 catalyst shows drastically deactivation after aging for 200 h at 650 °C. The maximum NO conversion of SCR-A2 catalyst falls to 95 % from 100 % after aging. It is apparently that the NO conversion has sharp falls at low temperature. The activity data of V_2O_5-WO_3-TiO_2 catalysts prove that it is only used in only SCR or DOC + SCR after-treatment system in which the gas exhaust temperature is below 550 °C and why

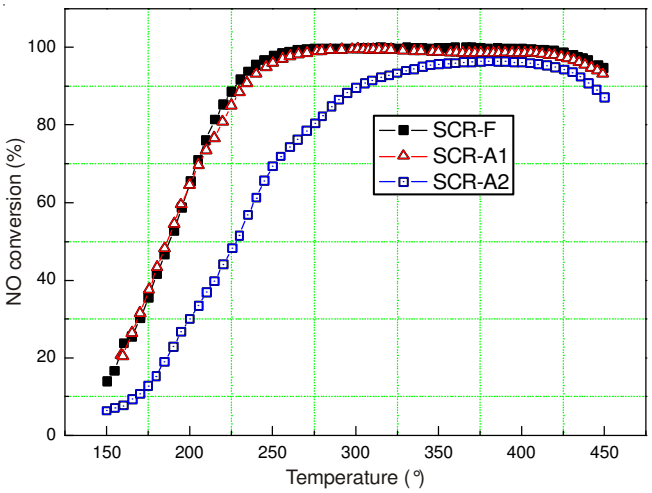

Fig. 1. NO conversion for fresh catalyst and aged catalyst

V_2O_5-WO_3-TiO_2 catalyst is insufficient for apply in DPF+SCR system, in which the DPF regeneration may raise the exhaust temperature to 650 °C.

Thermal analysis: The TG-DTA analyses of fresh SCR catalyst are given in Fig. 2. The TG curve shows the catalyst lose significantly weight in temperature range (51-300 °C) originated mainly from the evaporation of desorption water, followed by slight weight loss at about (310-627 °C). It is worth noting to mention that the weight loss of 0.8 % is accompanied with an endothermal peak at about (627-890 °C), in the literature[15] corresponding to the melting of vanadia. It is obvious deduction that the vanadia loading decrease resulting from vocalization above 600 °C, which is the one of the reasons for catalyst deactivation at 650 °C.

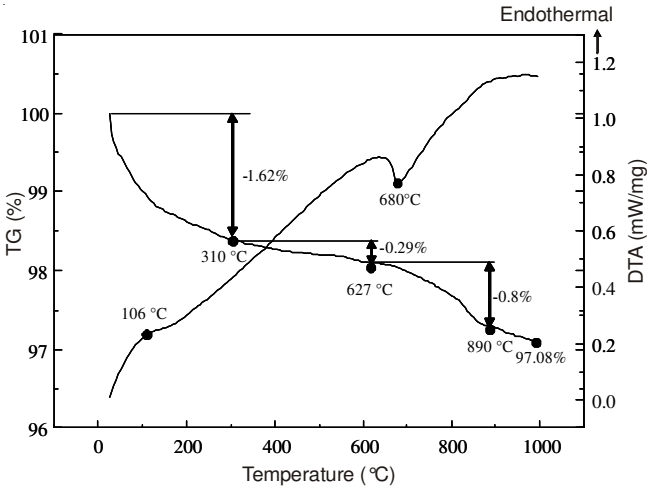

Fig. 2. TG-DTA curve of SCR-F

XRD analysis: The structure phase transformation of catalyst during thermal treatment is given in Fig. 3. There is only the TiO_2 is detected of all sample, No crystalline V_2O_5 and WO_3 was detected by XRD for all samples indicting that the structure of V_2O_5 and WO_3 is amorphous or that the loading is below the XRD detection limits[14,16]. The XRD patterns of SCR-F catalyst show the anatase is the main phase of TiO_2, which is accompanied with a small quality of rutile structure. The peaks of anatase TiO_2 become stronger and the peaks of

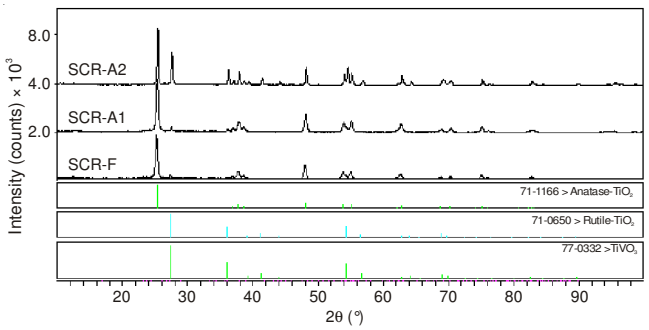

Fig.3 X-ray diffraction patterns of catalysts

rutile TiO_2 show little change after aging for 550 °C, indicating the transformation to rutile does not occur, only strengths the crystallinity of anatase TiO_2. For SCR-A2 catalyst, strong peaks for the rutile phase of TiO_2 are observed. the content of rutile become higher after aging for 650 °C, reflected the transformation of TiO_2 anatase into rutile. It is noted that the peaks of $TiVO_3$ appear for SCR-A2 catalyst, which is accordance with the TG date, V_2O_5 appears melting and interacts with TiO_2 above 600 °C.

Fig. 4 depicts the nitrogen adsorption desorption isotherm of SCR-F and SCR-A2.

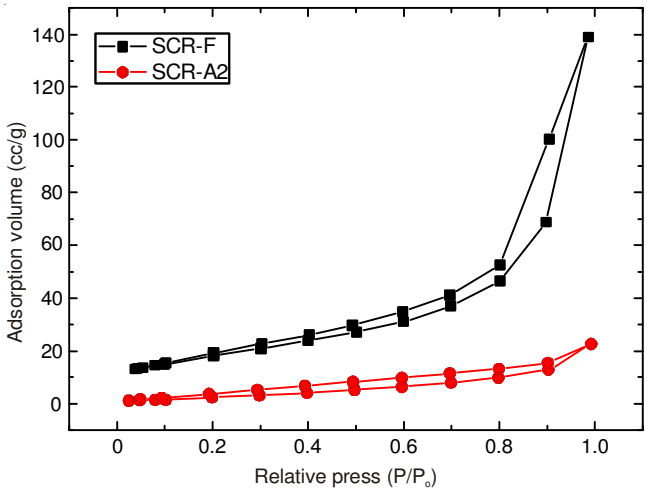

Fig. 4. Nitrogen adsorption-desorption isotherm of SCR-F and SCR-A2

BET analysis: Table-1 shows the surface area and pore volume of SCR-F and SCR-A1. After aging at 650 °C for 50 h, the surface area of V-W-TiO_2 catalyst remarkable decreases from 65.32 m^2/g to 10.58 m^2/g. Fig. 5 shows the majority of pore size in the range of 4-6 nm for fresh catalyst, which reflects the fresh catalyst is mesopore structure. The mesopore dramatically collapse because of the transformation of anatase to rutile for TiO_2.

Correspondingly, the average pore volume decreases from 0.21to 0.04 cc/g, reveals the reasons of surface area decreased of fresh catalyst. The pore structure analysis further describes

TABLE-1
PORE CHARACTERISTIC OF CATALYST

Item	BET (m^2/g)	Pore volume (cc/g)
SCR-F	65.32	0.21
SCR-A2	10.58	0.04

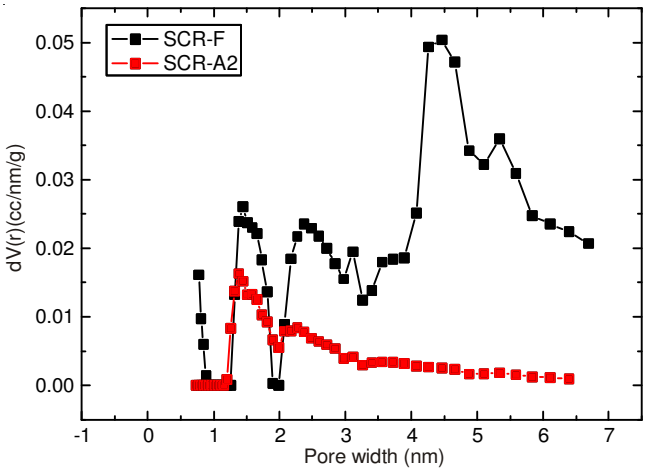

Fig. 5. Pore size distribution of catalyst

the catalytic activity deactivation mechanism that the reaction area decreased with a decrease of pore amount and pore volume.

Conclusion

V-W-TiO_2 catalyst shows excellent catalytic activity of SCR reaction, It has good thermal stability after aging at 550 °C for 50 h. when the aging temperature increased to 650 °C, the catalyst appears drastically deactivation. This is due to three changes of V-W-TiO_2 materials, including of vanadia content, active site amount and the phase of TiO_2.

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