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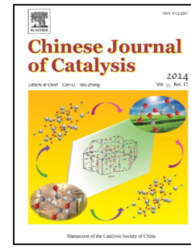

Article

Effect of V_2O_5/WO_3-TiO_2 catalyst preparation method on NO_x removal from diesel exhaust

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ABSTRACT

V_2O_5/WO_3-TiO_2 catalysts were prepared by conventional impregnation (VWTi-con) and ultrasound-assisted impregnation methods (VWTi-HUST). Their catalytic performance was tested for the selective catalytic reduction (SCR) of NO with NH_3. The effects of the preparation methods on the catalyst properties were studied. The catalysts were characterized by X-ray diffraction, scanning electron microscopy, Raman and X-ray photoelectron spectroscopy. Both structural investigation and NH_3-SCR activity showed that the preparation method had a strong effect on the thermal behavior of the V_2O_5/WO_3-TiO_2 catalysts. After a hydrothermal treatment, a significant loss of NO reduction activity was observed for the VWTi-con catalyst, which suffered severe sintering and even formed a rutile $V_xTi_{1-x}O_2$ solid solution, while the VWTi-HUST catalyst had the same good hydrothermal stability as a commercial catalyst, indicating that the VWTi-HUST catalyst can be used in a commercial diesel after-treatment system. The ultrasound-assisted impregnation method produced a stronger interaction between the vanadium species and WTi support, which stabilized the vanadium species in the reduced state.

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1. Introduction

Diesel vehicles have attracted a large market share for its benefits such as high power and good fuel economy [1]. However, the emission of nitrogen oxides (NO_x) by diesel vehicles is harmful to the environment and human health [2,3]. In order to eliminate NO_x pollution from diesel exhaust, ever-tightening emission regulations have been imposed in many countries.

One of the leading technologies for reducing NO_x emissions is the selective catalytic reduction by ammonia (NH_3-SCR), which has been extensively studied for lean NO_x control in stationary sources and diesel vehicle emission [4–6]. A catalyst with a high activity, broad operating temperature, and excellent hydrothermal stability is required for the NH_3-SCR technology [7–9]. The V_2O_5/WO_3-TiO_2 catalyst has been applied successfully for the exhaust treatment of heavy duty diesel engines for its high catalytic activity and selectivity, and superior resistance to sulfur poisoning [10,11]. Thus, the first choice for NH_3-SCR catalyst applied in the China stage IV standard is the developed V_2O_5/WO_3-TiO_2 catalyst.

TiO_2 in the form of the anatase phase is most widely used as the support of the V_2O_5/WO_3-TiO_2 catalyst due to its better electron transfer and superior resistance to sulfur poisoning [12,13]. Compared to other supports, anatase TiO_2 can remarkably improve the dispersion state of the VO_x species on the surface of catalysts [14]. The vanadium species on anatase

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TiO_2 include isolated VO_x species, aggregated VO_x species, and crystalline V_2O_5 [15]. The distribution of the VO_x species depends on the vanadium loading. Isolated and aggregated VO_x species are the main species at low loadings, while crystalline of V_2O_5 is formed as the loading increases [16]. WO_3 can stabilize the anatase phase of the TiO_2 support and increase the surface acidity of catalysts [17].

Although the V_2O_5/WO_3-TiO_2 catalyst has been widely used in stationary and mobile pollution sources, a major drawback is its thermal deactivation in the exhaust gas, which can reach over 650 °C under certain conditions [18,19]. The challenges for the automotive application of V_2O_5/WO_3-TiO_2 catalysts are high SCR activity and good thermal stability in the wide temperature range [20,21]. Composite supports have been used to improve the hydrothermal stability, such as TiO_2-SiO_2 [22,23], TiO_2-Al_2O_3 [24], and TiO_2-ZrO_2 [25]. Some researchers have improved the hydrothermal stability of vanadium catalysts by the formation of a rare earth metal vanadate, which can inhibit the formation of a rutile $V_xTi_{1-x}O_2$ solid solution [26]. V_2O_5/WO_3-TiO_2 catalysts have been prepared by different grafting sequences of the vanadium and tungsten onto the TiO_2, where the surface chemical properties and activity of the catalysts were shown to be independent of the sequence of the grafting sequence up to a monolayer of the catalyst [27]. However, studies on the effect of the V_2O_5/WO_3-TiO_2 catalyst preparation method on the fresh and hydrothermally aged SCR activities have not been systematic. Here, we prepared V_2O_5/WO_3-TiO_2 catalysts by conventional impregnation and ultrasound-assisted impregnation methods, and tested their catalytic performance for the SCR of NO with NH_3. The aim of the study was to understand and elucidate the deNO_x activity and deactivation behavior of the catalysts prepared by the different preparation methods.

2. Experimental

2.1. Catalyst preparation

WO_3-TiO_2 powder (WTi) was used as the support for preparing V_2O_5/WO_3-TiO_2 catalysts containing 10 wt% WO_3 and 3 wt% V_2O_5. The conventional impregnation method was as follows. WTi was impregnated with vanadium oxalate aqueous solutions followed by drying at 110 °C for 12 h and calcination at 500 °C for 5 h. After calcination, a measured amount of water was added to the as-prepared powder and mixed to form a well-mixed slurry. A cordierite support (cylinder, diameter 11 mm, length 22 mm, bulk 2.1 cm^3, 400 cell/cm^2) was coated by dipping it into the slurry. After each immersion, air was gently blown to eliminate excess slurry to achieve a homogeneous coating on the ceramic surface. Successive immersion of the cordierite in the slurry was performed to achieve the required loading of about 250 g/L. The monolithic catalyst was labeled as V_2O_5/WO_3-TiO_2-convention, which was also shortened to VWTi-con.

The ultrasound-assisted impregnation method was as follows. The WTi powder was put into the vanadium oxalate aqueous solution and thoroughly stirred, and then an ultrasonic treatment was applied for 1 h under a vacuum condition. Then, the sample was dried in a rotary vacuum dryer and calcined at 500 °C for 5 h. A cordierite support was coated followed the same procedure as above. This monolithic catalyst was labeled as V_2O_5/WO_3-TiO_2-HUST, which was shortened to VWTi-HUST.

In the experiment for comparing the different preparation methods, the vanadium oxalate aqueous solution was mixed with ammonium metavanadate (V_2O_5 3.0 wt%) with oxalic acid ($n(C_2H_2O_4\cdot 2H_2O):n(V_2O_5)$ = 3:1). All chemicals used were chemical grade. An imported industrial catalyst was used as the reference sample, and it was labeled as V_2O_5/WO_3-TiO_2-industrialization, which was shortened to VWTi-ind. To investigate the hydrothermal stability of the catalyst, the monolithic SCR catalyst was aged in a quartz tube reactor at 700 °C for 12 h with wet air containing 10% H_2O flowing at the rate of 1000 mL/min. The hydrothermally aged catalysts were labeled as A-VWTi-con, A-VWTi-HUST, and A-VWTi-ind.

2.2. Catalyst characterization

Powder X-ray diffraction (XRD) patterns were recorded on an X'Pert PRO X-ray diffractometer using Cu K_α irradiation. Scanning electron microscopy (SEM) images were obtained on a FEI Sirion 200 scanning electron microscope at 10.0 kV. X-ray photoelectron spectroscopy (XPS) analysis was carried out on an Axis Ultra DLD spectrometer with Al K_α irradiation. The binding of energies were calibrated using the C 1*s* peak at 284.7 eV as an internal standard. Raman spectra were acquired on LabRAM HR 800 equipped with a frequency-doubled Nd-YAG 532 nm laser.

2.3. NH_3-SCR activity

The activity of the monolithic SCR catalysts was measured in a fixed-bed stainless steel tubular reactor of 1.2 cm diameter and 80 cm length. The reactant gas composition was 1000 ppm NO, 1100 ppm NH_3, 5% O_2, and balance N_2. A 2.1 cm^3 monolithic catalyst was used in each test. The total flow rate was 1000 mL/min, that is, a GHSV by volume of 30 000 h^{-1} was obtained. The concentration of NO after the reaction was monitored by an exhaust analyzer (Foshan Analytical Instrument Co. Ltd., China, FGA-4100-5G). To avoid errors caused by the oxidation of NH_3, a NH_3 trap containing phosphoric acid solution was installed before the gas entered the exhaust analyzer.

3. Results and discussion

3.1. Characterization

The XRD pattens of the fresh and hydrothermally aged vanadium-based catalysts prepared by the different methods are shown in Fig. 1. On the fresh VWTi-con and VWTi-HUST catalysts, the peaks of anatase TiO_2 (2θ = 25.6°, 38.1°, and 48.2°) dominated the XRD pattern, and V_2O_5 and WO_3 diffraction peaks could not be detected, indicating that V_2O_5 and WO_3 were well dispersed as the amorphous oxide, or aggregated in

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