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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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ARTICLE INFO

Article history:

Received 20 June 2014

Accepted 2 September 2014

Published 20 December 2014

Keywords:

Selective catalytic reduction

Nitrogen oxide

Vanadium catalyst

Hydrothermal stability

Diesel engine

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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DOI: 10.1016/S1872-2067(14)60218-7 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 35, No. 12, December 2014

TiO₂ include isolated VO_x species, aggregated VO_x species, and crystalline V₂O₅ [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 V₂O₅ is formed as the loading increases [16]. WO₃ can stabilize the anatase phase of the TiO₂ support and increase the surface acidity of catalysts [17].

Although the V₂O₅/WO₃-TiO₂ 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 V₂O₅/WO₃-TiO₂ 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 TiO₂-SiO₂ [22,23], TiO₂-Al₂O₃ [24], and TiO₂-ZrO₂ [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}O₂ solid solution [26]. V₂O₅/WO₃-TiO₂ catalysts have been prepared by different grafting sequences of the vanadium and tungsten onto the TiO₂, 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 V₂O₅/WO₃-TiO₂ catalyst preparation method on the fresh and hydrothermally aged SCR activities have not been systematic. Here, we prepared V₂O₅/WO₃-TiO₂ catalysts by conventional impregnation and ultrasound-assisted impregnation methods, and tested their catalytic performance for the SCR of NO with NH₃. 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

WO₃-TiO₂ powder (WTi) was used as the support for preparing V₂O₅/WO₃-TiO₂ catalysts containing 10 wt% WO₃ and 3 wt% V₂O₅. 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 cm³, 400 cell/cm²) 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 V₂O₅/WO₃-TiO₂-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 ultrason-

ic 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 V₂O₅/WO₃-TiO₂-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 (V₂O₅ 3.0 wt%) with oxalic acid ($n(\text{C}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}):n(\text{V}_2\text{O}_5) = 3:1$). All chemicals used were chemical grade. An imported industrial catalyst was used as the reference sample, and it was labeled as V₂O₅/WO₃-TiO₂-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% H₂O 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 1s 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. NH₃-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 NH₃, 5% O₂, and balance N₂. A 2.1 cm³ 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 NH₃, a NH₃ trap containing phosphoric acid solution was installed before the gas entered the exhaust analyzer.

3. Results and discussion

3.1. Characterization

The XRD patterns 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 TiO₂ ($2\theta = 25.6^\circ$, 38.1° , and 48.2°) dominated the XRD pattern, and V₂O₅ and WO₃ diffraction peaks could not be detected, indicating that V₂O₅ and WO₃ were well dispersed as the amorphous oxide, or aggregated in

Fig. 1. XRD patterns of fresh and hydrothermally aged catalysts.

mini-crystallites that were too small to be detected by XRD. After hydrothermal aging, some TiO_2 transformation of anatase to rutile ($2\theta = 27.6^\circ, 36.3^\circ, 41.4^\circ$, and 54.5°) took place with the A-VWTi-con catalyst, while with A-VWTi-HUST, agglomeration of the WO_3 crystallites occurred but rutile TiO_2 peaks could not be detected.

The crystallite size and amount of anatase phase on the fresh and hydrothermally aged catalysts are shown in Table 1. The fresh VWTi-con and VWTi-HUST catalysts only exhibited the anatase phase, and the average crystallite size of anatase of both catalysts was in the range of 16–17 nm. After the hydrothermal treatment, the average crystallite size of the anatase of the VWTi-con catalyst increased from 16.4 to 52.3 nm, and the amount of anatase phase decreased from 100% to 65%. Growth of the anatase particles was less obvious with the VWTi-HUST catalyst, only increasing from 16.6 to 38.2 nm, and it still only had the anatase phase. The result indicated that the hydrothermal stability of the VWTi-HUST catalyst was better than the VWTi-con catalyst. In order to confirm the effect of preparation methods on the hydrothermal stability, we also investigated the average crystallite size and crystal phase composition of fresh and hydrothermally aged WTi, which was

Table 1

XRD parameters of the fresh and aged catalysts.

Sample	Phase composition	Crystallite size (nm)
WTi	Anatase	16.4
VWTi-con	Anatase	16.4
VWTi-HUST	Anatase	16.6
A-WTi	Anatase	23.4
A-VWTi-con	65% Anatase + 35% rutile	52.3
A-VWTi-HUST	Anatase	38.2

the support of VWTi-con and VWTi-HUST. The results indicated that the average crystallite size of the anatase of WTi only increased from 16.4 to 23.4 nm, and hydrothermal aging did not cause a phase transformation from anatase TiO_2 to the rutile phase. In addition, because VWTi-con and VWTi-HUST were essentially uniform in composition, this excluded the effect of the composition of the catalyst on the hydrothermal stability. These results proved that preparation method had an obvious effect on the hydrothermal stability of the vanadium based catalysts, namely, the phase transformation from anatase TiO_2 to the rutile phase was obviously suppressed by the ultra-sound-assisted impregnation method.

Fig. 2 displays the Raman spectra of the fresh and hydrothermally aged catalysts. As shown in Fig. 2(a), the Raman feature of the anatase structure ($398, 517$, and 639 cm^{-1}) dominated the spectra of all the fresh catalysts, which was in good agreement with the XRD data. In order to interpret the information for the surface structure of vanadium oxide and tungsten oxide, the Raman spectra with a smaller range of $1100\text{--}750 \text{ cm}^{-1}$ are also presented in Fig. 2. The Raman feature of the symmetrical V=O stretching mode and symmetrical W=O stretching mode at monolayer coverage ($965\text{--}990 \text{ cm}^{-1}$) was also observed on the fresh catalysts. Thus, the vibration peak at 969 cm^{-1} on the WTi was ascribed to the symmetrical W=O stretching mode; VWTi-con and VWTi-HUST displayed the peak at 982 cm^{-1} , which was ascribed to the overlap of the symmetrical V=O stretching mode and symmetrical W=O stretching mode at monolayer coverage. The vibration peak at 802 cm^{-1} appeared for all the samples, which was due to the crystalline WO_3 . In addition, there was no peak of crystalline

Fig. 2. Raman spectra of fresh catalysts (a) and hydrothermally aged $\text{V}_2\text{O}_5/\text{WO}_3\text{-TiO}_2$ catalysts (b).

V_2O_5 on VWTi-con and VWTi-HUST, indicating that the surface vanadium species were in a highly dispersed state. After the hydrothermal treatment, all the samples still exhibited the anatase structure. The Raman feature of rutile TiO_2 (445 and 616 cm^{-1}) could be only observed with the VWTi-con catalyst, indicating that for this catalyst, the hydrothermal treatment caused some transformation of anatase to rutile. In addition, compared to A-VWTi-con, A-VWTi-HUST showed a pronounced increase of the intensity of the peak (806 cm^{-1}) due to the crystalline WO_3 , indicating the growth of the crystalline phase during the hydrothermal treatment. An explanation is that the ultrasound-assisted impregnation method improved the interaction between the vanadium species and the WTi support, that is, the hydrothermal treatment caused the segregation of the WO_x species on the WTi support because of the relative weak interaction between the tungsten species and WTi support. The result indicated that the interaction between the vanadium species and the support strongly influenced the hydrothermal stability. It further showed that the ultrasound-assisted impregnation method played an important role in the hydrothermal stability of the catalyst.

SEM images of the fresh and hydrothermally aged VWTi-con and VWTi-HUST catalysts are shown in Fig. 3. There were no apparent differences between the VWTi-con and VWTi-HUST catalysts (Fig. 3(a) and (b)). After hydrothermally aged at 700 °C for 12 h, a significant change took place on the A-VWTi-con catalyst (Fig. 3(c)) where the catalytic particles were aggregated and developed to be extremely large. Combining this with the XRD and Raman results, it was concluded that this was because the phase transformation from anatase TiO_2 to the rutile phase took place during the hydrothermal aging process on the A-VWTi-con catalyst. The A-VWTi-HUST grew only slightly in size compared to the fresh catalyst (Fig. 3(d)).

The fresh and hydrothermally aged VWTi-con and VWTi-HUST catalysts were further analyzed using XPS to ob-

Fig. 4. V $2p_{2/3}$ XPS spectra of fresh catalysts (a) and hydrothermally aged $\text{V}_2\text{O}_5/\text{WO}_3\text{-TiO}_2$ catalysts (b).

tain information about the chemical state of the vanadium species. In order to make sure this showed the effect of different preparation methods on the dispersion of vanadium species, the XPS results of V $2p_{2/3}$ of the fresh and aged VWTi-ind catalysts are also displayed in Fig. 4. According to the previous findings [28,29], the core level of V $2p_{2/3}$ for V^{3+} , V^{4+} , and V^{5+} were in the ranges of 515.2–515.9, 515.9–516.7, and 516.7–517.9 eV, respectively. As shown in Fig. 4(a), the vanadium species on the VWTi-con catalyst were mainly in the high oxidation state (V^{5+} , 517.8 eV), and on the VWTi-HUST and VWTi-ind catalysts, they were primary in the reduced state of V^{3+} (515.6 eV) and V^{4+} (516.5 eV). Fig. 4(b) displays the XPS results of V $2p_{2/3}$ of hydrothermally aged catalysts. The A-VWTi-con catalyst displayed the highest V $2p_{2/3}$ BE value (518.4 eV) of all the catalysts, indicating an increase in the oxidation state of vanadium. This increase in the oxidation state of vanadium was primarily due to the formation of a rutile $\text{V}_x\text{Ti}_{1-x}\text{O}_2$ solid solution. Thus, the dispersion of the vanadium species was highly influenced by the preparation method, and the ultrasound-assisted impregnation method greatly improved the dispersion of the vanadium species and the interaction between vanadium species and the WTi support.

3.2. Effect of preparation methods on the activity of the $\text{V}_2\text{O}_5/\text{WO}_3\text{-TiO}_2$ catalysts

The NO reduction activity of the catalysts was examined using a feed gas containing 1000 ppm NO, 1100 ppm NH_3 , and 5% O_2 at the rate of 1000 mL/min. As shown in Fig. 5, the catalytic

Fig. 3. SEM images of fresh and hydrothermally aged catalysts. (a) VWTi-con; (b) VWTi-HUST; (c) A-VWTi-con; (d) A-VWTi-HUST.

Fig. 5. Catalytic performance of fresh and hydrothermally aged V_2O_5/WO_3-TiO_2 catalysts.

performance of all the fresh vanadium catalysts was about the same. It was reported that the surface structure of vanadium species present in the catalyst has a pronounced effect on the activity and the selectivity for the NH_3 -SCR [30,31]. From the XRD, SEM, and Raman results, the vanadium species were well dispersed on the VWTi-con and VWTi-HUST catalysts, which explained why fresh VWTi-con and VWTi-HUST possessed the same NH_3 -SCR activity.

In order to investigate the effects of hydrothermal aging on the catalytic activity, the vanadium catalysts were further treated at 700 °C for 12 h with flowing wet air containing 10% H_2O . Fig. 5 displays the NO conversion of the hydrothermally aged catalysts. After hydrothermal treatment, a significant loss of NO reduction activity, in highly varying extents, was observed for the A-VWTi-con catalyst. More importantly, the NO conversion was negative at a high temperature (> 400 °C) due to the formation of rutile $V_xTi_{1-x}O_2$, which was caused by the parallel oxidation of NH_3 by O_2 [19]. The trend of the NO conversion curve of A-VWTi-HUST and A-VWTi-ind was much better than that of A-VWTi-con. This indicated that the VWTi-HUST catalyst was much more robust than the VWTi-con catalyst and had a better resistance to the harsh hydrothermal treatment. The hydrothermal stability of the VWTi-HUST catalyst was the same as the commercial VWTi-ind catalyst, indicating the feasibility of its application in a commercial diesel after-treatment system. The Raman and XPS results showed that the ultrasound-assisted impregnation method greatly improved the interaction between the vanadium species and the WTi support, and stabilized the vanadium species in the reduced state. Combining with the XRD, SEM, and Raman results, it was concluded that severe sintering of the anatase TiO_2 occurred, and even a phase transition was observed on the A-VWTi-con catalyst due to the formation of rutile $V_xTi_{1-x}O_2$. It is known that the transformation to rutile is detrimental for the active 'monolayer' of vanadium species on the anatase surface resulting in a degradation of the catalytic performance [18]. For the A-VWTi-HUST catalyst, the TiO_2 sintering and phase transformation were obviously suppressed by the ultrasound-as-

sisted impregnation method. It was critical for the dispersion of the active vanadium species on the hydrothermally aged catalyst [31]. Therefore, the reducibility of the vanadium oxide species and the strong interaction played a critical role in determining the hydrothermal stability of the vanadium-based catalysts. It further proved the effect of the preparation method on the performance of V_2O_5/WO_3-TiO_2 catalyst.

4. Conclusions

NH_3 -SCR activity over fresh and hydrothermally aged V_2O_5/WO_3-TiO_2 catalysts prepared using the conventional impregnation and ultrasound-assisted impregnation methods was studied. The vanadium species were well dispersed on the fresh VWTi-con and VWTi-HUST catalysts. After hydrothermal treatment, a significant loss of NO reduction activity was observed for the VWTi-con catalyst, which experienced severe sintering and even formed a rutile $V_xTi_{1-x}O_2$ solid solution. The VWTi-HUST catalyst had better resistance to the harsh hydrothermal treatment and had the same good hydrothermal stability as a commercial VWTi-ind catalyst. By comparing the impregnation methods, it was concluded that 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. A correlation was found between the preparation method and hydrothermal stability of the V_2O_5/WO_3-TiO_2 catalyst.

Acknowledgments

Thankfulness is expressed for the spectroscopic analysis to the Analytical and Testing Center, Huazhong University of Science and Technology, Wuhan, China.

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Graphical Abstract

Chin. J. Catal., 2014, 35: 0–0 doi: 10.1016/S1872-2067(14)60218-7

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

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V_2O_5/WO_3 - TiO_2 catalysts were prepared by the convention impregnation and ultrasound-assisted impregnation methods. The hydrothermal stability of the catalysts depended on the preparation method. The catalyst prepared by ultrasound-assisted impregnation showed better hydrothermal stability.

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制备方法对 V_2O_5/WO_3 - TiO_2 催化剂脱除柴油车尾气中 NO_x 的影响

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摘要: 分别采用普通浸渍法(VWTi-con)和超声辅助浸渍法(VWTi-HUST)制备了 V_2O_5/WO_3 - TiO_2 催化剂, 并用X射线衍射、扫描电镜、拉曼光谱和X射线光电子能谱等技术对催化剂进行了表征, 评价了水热老化前后两种催化剂的 NH_3 -SCR脱除模拟柴油车尾气中 NO_x 的反应活性, 并与国外成熟商品催化剂进行了比较. 结果表明, 制备方法可影响 V_2O_5/WO_3 - TiO_2 催化剂的水热稳定性, VWTi-con催化剂老化后几乎完全失活, 而VWTi-HUST具有优异的水热稳定性, 与国外成熟商品催化剂性能相当. 与传统浸渍法相比, 超声辅助浸渍法增强了活性物种和载体的相互作用, 提高了活性组分的分散性等. 采用该法制备的VWTi-HUST催化剂将具有较强的商业应用性; 台架试验正在进行中, 以期满足柴油车国IV排放标准的要求.

关键词: 选择性催化还原; 氮氧化合物; 钒基催化剂; 水热稳定性; 柴油机

收稿日期: 2014-06-20. 接受日期: 2014-09-02. 出版日期: 2014-12-20.

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1. 前言

柴油车以其燃油经济性和良好的动力逐渐被消费者认可,因而在汽车市场中所占份额不断增加^[1].与汽油车相比,柴油车尾气中主要的污染物为氮氧化物(NO_x),严重危害了生态环境和人类健康^[2,3].为了减少柴油车污染物排放,世界各国制定和实施了严格的排放法规和标准,我国重型柴油车排放标准国III、国IV和国V已于2006年发布,国IV排放标准已于2014年7月1日实施.

选择性还原(SCR)是一种净化贫燃条件下柴油车尾气中 NO_x 的主流技术之一,具有燃油经济性高、脱硝效率高和对柴油含硫量要求低等优势^[4–6].鉴于柴油车国IV阶段排放标准已经实施以及我国目前的燃油品质,SCR成为满足国IV排放标准的首选技术路线.该技术的核心是开发具有高活性、宽操作温度窗口和优异水热稳定性的催化剂,以期应用于柴油车尾气 NO_x 催化净化^[7–9].钒基催化剂具有脱硝效率高、选择性好、抗硫中毒性能高等优点,在欧洲柴油车脱硝早期得到广泛应用^[10,11].借鉴欧洲重型柴油车SCR催化剂发展经验,结合我国国情,国IV排放标准将采用成熟的 $\text{V}_2\text{O}_5/\text{WO}_3\text{-TiO}_2$ 催化剂体系作为现阶段首选的 $\text{NH}_3\text{-SCR}$ 催化剂.

$\text{V}_2\text{O}_5/\text{WO}_3\text{-TiO}_2$ 催化剂的载体为锐钛矿型 TiO_2 ,具有良好的电子传递能力和高抗硫中毒性能^[12,13];与其他载体相比,钒物种在锐钛矿型 TiO_2 表面分散良好,并具有丰富的表面分布态^[14].研究表明^[15], V_2O_5 在催化剂表面存在孤立的 VO_x 物种、聚合态 VO_x 物种以及结晶态 V_2O_5 .Watches^[16]认为,当钒负载量低时,催化剂表面主要存在孤立的 VO_x 物种;随着钒负载量增加,催化剂表面出现聚合态 VO_x 物种,在达到单层分散阈值后形成结晶态 V_2O_5 .根据文献报道^[17], WO_3 的掺杂有助于提高 TiO_2 载体的热稳定性,抑制锐钛矿型 TiO_2 的烧结和晶相转换,同时增加催化剂的比表面积和表面酸性,改善催化剂表面V物种的分散状态.

尽管 $\text{V}_2\text{O}_5/\text{WO}_3\text{-TiO}_2$ 催化剂在固定源和移动源脱硝中得到了广泛应用,但在实际应用中存在水热稳定性差的问题^[18,19].随着柴油车后处理系统的集成,柴油车尾气温度可高达650 °C以上,钒基催化剂的水热稳定性限制了其在汽车上的应用^[20,21].针对该催化剂体系的缺点,许多研究者对钒基催化剂进行了大量的改性工作,包括载体改性和活性组分改性,并取得了一些阶段性成果.一些研究者采用复合氧化物为载体,如 $\text{TiO}_2\text{-SiO}_2$ ^[22,23], $\text{TiO}_2\text{-Al}_2\text{O}_3$ ^[24]和 $\text{TiO}_2\text{-ZrO}_2$ ^[25]等,提高了

钒基催化剂载体的热稳定性;还通过稀土金属和 VO_x 物种生成稀土金属钒酸盐,固化了催化剂表面的 VO_x 物种,阻止其进入 TiO_2 体相,从而有效抑制了 $\text{V}_x\text{Ti}_{1-x}\text{O}_2$ 固溶体的生成,提高了钒基催化剂的水热稳定性^[26].Reiche等^[27]考察了活性组分浸渍顺序对 $\text{V}_2\text{O}_5\text{-WO}_3\text{-TiO}_2$ 催化剂的影响,发现不同浸渍顺序对催化剂表面V物种的单层分散没有影响.

对于 $\text{V}_2\text{O}_5/\text{WO}_3\text{-TiO}_2$ 催化剂,目前国内的研究主要集中在催化剂改性、碱金属中毒机制和活性组分的分散状态等方面,关于制备方法对钒基催化剂水热稳定性影响的报道很少.另一方面,国内车用催化剂市场基本由国外公司垄断,如巴斯夫、庄信万丰和优美科公司等.为避开国外 $\text{NH}_3\text{-SCR}$ 净化柴油车尾气中 NO_x 的技术壁垒,开发生产具有自主知识产权的SCR钒基脱硝催化剂迫在眉睫.

本文采用普通浸渍法和超声辅助浸渍法制备了 $\text{V}_2\text{O}_5/\text{WO}_3\text{-TiO}_2$ 催化剂,并用X射线衍射(XRD)、扫描电镜(SEM)、拉曼光谱(Raman)和X射线光电子能谱(XPS)等技术对催化剂进行了表征,研究了不同制备方法对钒基催化剂性能、结构和水热稳定性的影响,评价了水热老化前后催化剂 $\text{NH}_3\text{-SCR}$ 脱除模拟柴油车尾气中氮氧化物的反应活性,并与国外成熟的商品钒基催化剂性能进行了比较,对于开发生产具有自主知识产权的SCR钒基脱硝催化剂具有重要意义.

2. 实验部分

2.1. 催化剂制备

采用传统浸渍法制备催化剂时,按照 $\text{V}_2\text{O}_5\text{:TiO}_2$ 质量比3%称取一定量的偏钒酸铵溶于草酸溶液中($\text{C}_2\text{H}_2\text{O}_4\cdot 2\text{H}_2\text{O}$ 和 V_2O_5 摩尔比为3:1),将经前期预处理的 WO_3/TiO_2 载体浸入上述溶液中,恒温剧烈搅拌2 h,将所得样品在110 °C干燥12 h后,于500 °C焙烧5 h.将制得的催化剂粉末与少量水混合,制备浆液,涂覆于堇青石蜂窝陶瓷基体小样(圆柱体,直径1.1 cm,高2.2 cm,总体积2.1 cm^3 ,400 cell/ cm^2),催化剂涂覆量约为250 g/L,所得整体式催化剂记为VWTi-con.

采用超声辅助浸渍法制备催化剂时,将经前期预处理的 WO_3/TiO_2 载体放入超声波发生器中,在真空下浸入上述偏钒酸铵草酸溶液中,开启超声波发生器1 h,然后采用旋转真空干燥,500 °C焙烧5 h.整体式催化剂制备过程如上所述.所得催化剂记为VWTi-HUST.上述两个催化剂中 WO_3 和 V_2O_5 的负载量分别为10%和3%.

在上述制备过程中,前驱体溶液是由偏钒酸铵按一定比例(V_2O_5 质量分数为2.5%)溶解于1 mol/L草酸溶液制得.为了比较,选用国外某品牌成熟的 $\text{V}_2\text{O}_5/\text{WO}_3\text{-TiO}_2$ 催化剂作为标样,命名为VWTi-ind.

上述三个催化剂在含10% H_2O 的空气(1000 mL/min)中于700 °C水热老化12 h,即得相应老化催化剂样品A-VWTi-con, A-VWTi-HUST和A-VWTi-ind.

2.2. 催化剂表征

XRD实验在X'Pert PRO型X射线衍射仪上进行,采用 $\text{Cu K}\alpha$ 作辐射光源.催化剂形貌观察在FEI Sirion 200型场发射SEM仪上完成. XPS在VG Multilab 2000系统上记录,采用 $\text{Al K}\alpha$ 射线为光源,功率为300 W. Raman光谱测试在LabRAM HR800激光共焦拉曼光谱仪上进行, Nd-YAG激光器,激光波长532 nm.

2.3. 催化剂评价

催化剂活性评价在自制气固催化反应装置上进行,催化剂体积为2.1 mL,反应气体组成为1000 ppm NO, 1100 ppm NH_3 和5% O_2 , N_2 为载体,总流量为1000 mL/min,反应空速为30 000 h^{-1} .反应进出口气体NO浓度由FGA-4100型烟气分析仪(佛山佛分环保仪器检测设备有限公司)在线检测,为避免未反应的 NH_3 影响测试结果,待测气体进入分析仪前先经过装有浓磷酸的氨阱.为了确保活性数据不受吸附影响,在每个测试点稳定1 h后进行数据记录,催化剂活性以NO转化率衡量.

3. 结果与讨论

3.1. 催化剂表征结果

图1为不同方法制备的钒基催化剂水热老化前后的XRD谱.由图可见,两种新鲜催化剂的XRD谱没有明显差别,均出现了锐钛矿型 TiO_2 的特征衍射峰,而未出现 V_2O_5 和 WO_3 晶体的特征衍射峰,说明在VWTi-con和VWTi-HUST催化剂中,钒和钨的氧化物在载体表面均匀分散.水热老化后,A-VWTi-con催化剂表面出现了金红石型 TiO_2 的特征衍射峰,表明该催化剂在水热老化过程中, TiO_2 载体由锐钛矿型转化为金红石型;在A-VWTi-HUST催化剂中检测到 WO_3 晶体的特征衍射峰,但是没有金红石型 TiO_2 的特征衍射峰,表明该催化剂具有较高的结构稳定性.

表1为新鲜和水热老化的WTi载体、VWTi-con和VWTi-HUST催化剂中 TiO_2 晶型的组成和 TiO_2 晶粒的大小.由表可见,两种催化剂的载体WTi粉体水热老化前后的晶粒尺寸由16.4 nm仅增加至23.4 nm,表明在苛

刻的水热老化条件下WTi载体具有优异的水热稳定性,两种催化剂不同的水热稳定性和载体无关联.新鲜VWTi-con和VWTi-HUST催化剂的 TiO_2 晶粒尺寸为16–17 nm.经过苛刻的水热老化后,A-VWTi-con催化剂中 TiO_2 晶粒尺寸迅速增大至52.3 nm,同时出现33%的金红石晶型;但A-VWTi-HUST催化剂的 TiO_2 晶粒尺寸仅增加到38.2 nm,且未发生晶型转换,可见制备方法影响了钒基催化剂的水热稳定性.

图2为不同方法制备的钒基催化剂和WTi载体老化前后的Raman谱.由图可见,WTi载体和所有新鲜的钒基催化剂均出现了锐钛矿型 TiO_2 的特征振动峰(398, 517, 639 cm^{-1}),同时在965–990 cm^{-1} 范围内出现了振动峰.根据文献报道,该区域振动峰归属为催化剂表面的 VO_x 和 WO_x 中 V=O 和 W=O 的对称伸缩振动.因此,WTi载体在969 cm^{-1} 的振动峰归属为表面 W=O 的振动;VWTi-con和VWTi-HUST催化剂由于表面 V=O 和 W=O 的共同振动作用使振动峰迁移至982 cm^{-1} .同时在WTi载体、VWTi-con和VWTi-HUST催化剂表面检测到晶态 WO_3 较弱的特征振动峰(802 cm^{-1}),进一步证明了 WO_3 在催化剂表面以微晶状态存在;在VTi, VWTi-con和VWTi-HUST催化剂表面未检测到晶相 V_2O_5 的 V=O 特征振动峰,表明催化剂表面的 V_2O_5 均以高度分散状态存在.如图2所示,A-VWTi-con催化剂表面出现了锐钛矿型 TiO_2 (445和616 cm^{-1})的特征振动峰,表明VWTi-con催化剂在水热老化过程中载体 TiO_2 晶相发生转变,这与XRD结果相符.与A-VWTi-con相比,A-VWTi-HUST表面出现较强的 WO_3 特征振动峰(806 cm^{-1}),表明在水热老化过程中催化剂表面的 WO_x 聚合为结晶态.由于超声辅助浸渍法可以提高钒物种和WTi载体相互作用力,因而抑制了钒物种在水热老化过程中团聚,从而提高了钒基催化剂的水热稳定性,进一步证明了制备方法影响了钒基催化剂的水热稳定性.

图3为不同方法制备的钒基催化剂老化前后的SEM照片.由图3(a)和(b)所示,VWTi-con和VWTi-HUST催化剂样品的形貌没有明显差别.图3(c)和(d)为在700 °C水热老化12 h后的A-VWTi-con和A-VWTi-HUST催化剂的SEM照片.可见,A-VWTi-con催化剂发生了明显的团聚现象,而A-VWTi-HUST催化剂粒径增长不大,与XRD和Raman结果相符,进一步证明了VWTi-HUST催化剂具有较强的抗老化能力.

为了确定制备方法对钒基催化剂表面钒物种的影响,图4对比了商品催化剂和不同制备方法的钒基催化

剂老化前后的V $2p_{3/2}$ XPS谱. 根据文献报道^[28,29], 钒基催化剂中, V^{3+} 的结合能位于515.2–515.9 eV, V^{4+} 的结合能位于515.9–516.7 eV, V^{5+} 的结合能位于516.7–517.9 eV. 如图4(a)所示, VWTi-con催化剂表面的 VO_x 物种主要为 V^{5+} (517.8 eV), 而VWTi-HUST催化剂表面以低价态的 V^{3+} (515.7 eV) 和 V^{4+} (516.5 eV) 物种为主. 另外, VWTi-HUST催化剂表面的 VO_x 物种和VWTi-ind催化剂的相同, 均以还原态 VO_x 物种为主. 图4(b)为不同方法制备的钒基催化剂和商品催化剂老化后的V $2p_{3/2}$ XPS谱. 如图所示, 所有催化剂表面的V $2p_{3/2}$ 的特征峰向高结合能方向迁移, 说明催化剂表面的 VO_x 物种在水热老化过程中发生了团聚, 以高价态 VO_x 物种存在于催化剂表面, 其中A-VWTi-con显示出最高的V $2p_{3/2}$ 结合能(518.4 eV), 表明该催化剂 VO_x 物种的V–O趋于更高配位, 即生成金红石型 $V_xTi_{1-x}O_x$ 固溶体. 综上, 不同制备方法影响了催化剂表面 VO_x 物种的存在状态, VWTi-con表面主要是 V^{5+} 活性物种, 而VWTi-HUST表面具有丰富的 VO_x 物种, 且以低价还原态为主; 水热老化后, 与A-VWTi-HUST和A-VWTi-ind催化剂相比, A-VWTi-con催化剂表面的 VO_x 物种团聚更为严重.

3.2. 催化剂的 NH_3 -SCR活性

图5为新鲜和老化的钒基催化剂上 NH_3 -SCR反应的NO转化率. 由图可见, 三种新鲜催化剂的SCR活性几乎没有差异, 在300–400 °C时NO转化率平均在90%以上, 随着反应温度的升高, NO转化率先升高, 达到最高转化率并保持一段温度后下降. 结合前文可知, 新鲜的VWTi-con和VWTi-HUST催化剂载体为锐钛矿, 活性组分分散均匀, 两种催化剂表面具有丰富的 VO_x 物种. 以上结果说明, 制备方法对新鲜催化剂的 NH_3 -SCR活性没有影响.

由图5还可以看出, 老化后的A-VWTi-con催化剂几乎完全失活, 在整个评价温度范围内的最高转化率不到

15%, 在高温(> 400 °C)时甚至为负值. 这是由于生成的金红石型固溶体促进了 NH_3 的氧化反应生成NO或 NO_2 ^[19]. 而A-VWTi-HUST催化剂具有较高的水热稳定性, 在375–400 °C范围内NO转化率达到60%左右, 其水热老化性能和商品催化剂VWTi-ind基本相同, 表明该催化剂具有较强的商业应用性, 其台架试验正在进行中, 以期满足国IV排放标准的要求.

由前面讨论可知, 超声辅助浸渍法增强了活性钒物种和载体的相互作用, 提高了活性组分的分散性, 保持了其还原性. 钒基催化剂的表面钒物种影响了催化剂的 NH_3 -SCR活性、 N_2 选择性和水热稳定性^[30,31]. 因此, 水热老化后, A-VWTi-con催化剂载体 TiO_2 发生了烧结和晶相转换, 表面分散的 V^{5+} 物种发生团聚, 生成固溶体, 导致其活性几乎完全失去. 而A-VWTi-HUST催化剂载体的烧结和晶相转换得到了有效抑制, 表面部分还原性 VO_x 物种团聚生成高价态 V^{5+} , 因此在700 °C水热老化的苛刻条件下仍具有优异的水热稳定性.

4. 结论

采用普通浸渍法和超声辅助浸渍法制备了 V_2O_5/WO_3-TiO_2 催化剂, 并考察了水热老化前后催化剂的 NH_3 -SCR脱除模拟柴油车尾气中氮氧化物的反应活性. 结果表明, 不同方法制备的新鲜催化剂具有相同的 NH_3 -SCR活性. 但是制备方法可影响催化剂的水热稳定性, 水热老化后VWTi-con催化剂几乎完全失活, 而VWTi-HUST具有和商品催化剂VWTi-ind相同的水热稳定性. 与传统浸渍法相比, 超声辅助浸渍法增强了活性钒物种和载体的相互作用, 提高了活性组分的分散性, 保持了其还原性等, 因此采用该法制备的VWTi-HUST具有优异的水热稳定性, 表现出较强的商业应用价值, 其后续台架试验正在进行中, 以期满足国IV排放标准的要求.

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