

Article

Study of the V₂O₅-WO₃/TiO₂ Catalyst Synthesized from Waste Catalyst on Selective Catalytic Reduction of NO_x by NH₃[†]

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Abstract: V₂O₅-WO₃/TiO₂ catalysts were synthesized from waste selective catalytic reduction (SCR) catalyst through oxalic acid leaching and impregnating with various V₂O₅ mass loadings. The denitration (deNO_x) activity and physiochemical properties of the catalysts were investigated. All the catalysts were characterized by N₂ adsorption/desorption, Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy, and H₂-temperature programmed reduction. The evaluation result revealed that the deNO_x activity of newly synthesized catalyst with 1.0% V₂O₅ was almost recovered to the level of fresh catalyst, with NO conversion being recovered to 91% at 300 °C, and it also showed a good resistance to SO₂ and H₂O. The characterization results showed that the decrease of impurities, partial recovery of the V⁴⁺/V⁵⁺ ratio, and increased reducibility were mainly responsible for the recovery of catalytic activity.

Keywords: V₂O₅-WO₃/TiO₂ catalyst; leaching; oxalic acid; deNO_x activity

1. Introduction

Selective catalytic reduction (SCR) of nitrogen oxides with ammonia is one of the most effective methods for eliminating the hazardous NO_x emission from stationary sources [1]. The honeycomb monolith V₂O₅-WO₃/TiO₂ catalyst is widely used for commercial processes because of its high activity and SO₂ resistance [2]. For the V₂O₅-WO₃/TiO₂ catalyst, anatase TiO₂ acts as a carrier, V₂O₅ is the active component, and WO₃ performs as the promoter to stabilize the catalyst and prevents the catalyst from sintering. In coal-fired power plants, the SCR catalyst suffers from gradual deactivation during the operation period because of poisoning, sintering, fouling, surface masking, attrition/crushing, and loss of vanadium or change in ratio value of the vanadium in different valence states [3–8].

Deactivated catalysts that retain a relatively intact monolith structure and low activity are always liable for regeneration by special regeneration equipment. A typical regeneration process generally involves mechanical blowing (dust removal), depth cleaning (toxic component elimination and inner channel dredging), active component impregnation, drying, and calcination [9–11]. By contrast, deactivated catalysts that involve physical breakage or attrition of the monolith and low activity are supposed to be disposed of as waste. Reportedly, 70%–80% of deactivated SCR catalysts could be

regenerated, but the regeneration time is limited, and all deactivated SCR catalysts will eventually end up as waste [12].

In China, waste SCR catalyst was classified as hazardous waste in 2014, and effective highly cautious disposal is a matter of great urgency [13]. To date, researchers are mainly focused on a variety of recycling and reuse technologies including mineral filter applications, incorporation into a wet-bottom boiler slag, cement kiln co-processing, iron/steel-making applications [14,15], and its use in fresh catalyst manufacture and materials recovery [12,16,17]. Therein, the reuse of waste SCR catalysts to synthesize fresh SCR catalysts is supposedly an economical and high resource utilization method [15]. However, the direct utilization of waste SCR catalysts in the synthesis of fresh SCR catalysts invariably results in low catalytic activity. This reason is due to the powder of titanium and tungsten more easily agglomerating under the effect of binder during mixing, leading to an uneven distribution [18]. In addition, the deposited sulfates and metals, such as Fe, K, and Na, are toxic to catalysts, and reduce their activity significantly. Moreover, the valence alternation of activated vanadium results in the decrease of the concentration of V^{4+} species, so the catalyst activity cannot recover to the level of the fresh catalyst only by only removing the deposited contaminants.

Therefore, prior to reuse, cleaning of waste SCR catalysts should be required. At present, various aqueous solutions including acids, alkalis, and salts have been proposed for washing waste SCR catalyst. Diluted H_2SO_4 is proven to be effective in recovery of the activity of waste catalyst by removing alkali metals and alkaline earth metals, and recovering the porosity [19,20]. To our knowledge, the alkali solution might be more effective in dissolving sulfates [21]. Yu et al. [21] investigated the alkali washing of deactivated commercial SCR catalyst, which could effectively remove the deposited $Al_2(SO_4)_3$ and recover porosity. However, the element Na deposited on the catalyst during alkali washing may exert an adverse impact on catalyst activity. With this consideration, alkali washing is always followed by acid washing. Washing by dilute NaOH and HNO_3 solutions in sequence is found to be more effective with respect to activity recovery [22]. Furthermore, washing with ammonium salt solutions, such as NH_4Cl and $(NH_4)_2SO_4$ solution, are also found to be an effective method to regain $deNO_x$ activity [20,23].

Among these aqueous solutions, oxalic acid (OA), a strong organic acid, is effective in removing alkali metals, Fe, and other contaminants. It has been widely used in the regeneration of deactivated catalysts. Christou et al. [24] found oxalic acid was effective in removing P- and S-containing compounds from aged commercial three-way catalysts, and the investigation of oxalic acid in removing Pb, Zn, Ca, Mn, Fe, Cu, and Ni metal contaminants was also performed [25,26]. On the other hand, OA is reducing and has been used as a complexing agent to selectively extract vanadium from the spent catalyst [27], so vanadium in different valence states can be eluted forcedly by aqueous OA solution. In this work, the valence of vanadium changed in the waste catalyst, and resulted in the decrease of V^{4+}/V^{5+} ratio. In addition, Fe was also significantly deposited on the catalyst, resulting in the increase of the SO_2 oxidation rate [28]. OA solution was reported to have a high extract efficiency of V and Fe due to its strong acidity and good complexing effects [29]. More significantly, the obtained leaching residue is mainly anatase TiO_2 , which can be reused as a carrier for the synthesis of new SCR catalyst.

In this work, the $V_2O_5-WO_3/TiO_2$ catalysts were synthesized from waste SCR catalyst after oxalic acid leaching and impregnating with various V_2O_5 mass loadings. The $deNO_x$ activity and physiochemical properties were investigated. The surface structural, textural, and redox properties of the fresh waste and resynthesized $V_2O_5-WO_3/TiO_2$ catalysts were characterized by N_2 adsorption/desorption, Fourier transform infrared (FT-IR) spectroscopy, X-ray photoelectron spectroscopy (XPS), and H_2 -temperature programmed reduction (H_2 -TPR).

2. Results and Discussion

2.1. Characteristics of the Fresh and Waste SCR Catalyst

The main compositions of the fresh (donated as Fresh) and waste (donated as Waste) SCR catalysts are listed in Table 1. Compared with the fresh catalyst, waste catalyst showed 20% lower V content. Moreover, the concentrations of Al, Si, Ca, Fe, K, and Na increased to varying degrees. Notably, the K concentration was 10 times higher than that in fresh catalyst. In addition, Fe and Al elements also evidently accumulated in the waste catalyst, with the concentrations being six and two times higher than those of the fresh catalyst, respectively. Evidently, the waste catalyst could not be directly reused by blending with fresh catalyst, because the deposited alkali metals and alkaline earth metals exert an adverse effect on catalytic activity. Therefore, the waste catalyst was first washed with OA solution, and the compositions of OA leaching residue are also presented in Table 1. The contents of alkali metals (K, Na) and Fe in OA leaching residue markedly declined and were similar to that in the fresh catalyst. In addition, the contents of Al and Ca also dropped by different degrees, and approximately 44% of Al and 17% of Ca were removed. A large percentage of V was dissolved at the same time.

Table 1. Main compositions of the fresh, waste V_2O_5 - WO_3 / TiO_2 catalysts and oxalic acid (OA) leaching residue as analyzed by an inductively coupled plasma atomic emission spectrometer (ICP-AES).

Sample	Composition (wt %)								
	Ti	V	W	Al	Si	Ca	Fe	K	Na
Fresh	55.04	0.39	3.48	0.44	0.87	0.84	0.04	0.02	0.07
Waste	51.88	0.31	4.57	0.92	0.92	0.90	0.24	0.24	0.13
OA leaching residue	52.42	0.12	3.94	0.52	1.02	0.75	0.07	0.04	0.03

Figure 1 displays the X-ray diffraction (XRD) patterns of the fresh, waste, and OA leaching residue. Similar to the fresh and waste catalysts, the anatase type TiO_2 carrier was not destroyed after leaching, and the obtained residue was mainly composed of anatase TiO_2 .

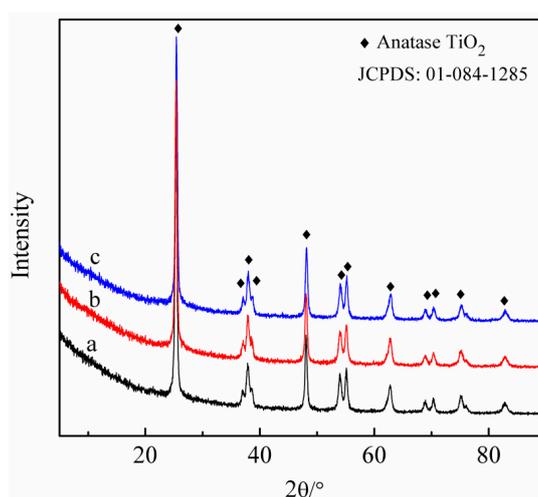


Figure 1. X-ray diffraction (XRD) patterns of the (a) Fresh, (b) Waste, and (c) OA leaching residue.

Based on the results of the analysis of compositions and XRD, the OA leaching residue was expected to synthesize the new V_2O_5 - WO_3 / TiO_2 catalyst after impregnation of the active components. So the V_2O_5 - WO_3 / TiO_2 catalysts loaded with 0.5%, 1.0%, and 1.5% V_2O_5 were resynthesized from the OA leaching residue.

2.2. Catalytic Activity Test

The deNO_x activity profiles of the fresh, waste, and resynthesized (donated as Re-*x*%, where *x* was the overall V₂O₅ content in the catalyst after oxalic acid leaching and vanadium impregnation) V₂O₅-WO₃/TiO₂ catalysts are presented in Figure 2. The waste catalyst showed a similar deNO_x activity to the fresh catalyst at temperatures exceeding 350 °C, but exhibited a lower activity in the temperature range of 150–350 °C. In particular, the NO conversion of the waste catalyst was 80% at 300 °C, which was less than that of the fresh catalyst (96%). Furthermore, a direct impregnation of additional 0.2% V₂O₅ on a waste catalyst was tested, but no improvement in the NO reduction efficiency was observed (Figure S1). Therefore, V₂O₅-WO₃/TiO₂ catalysts were resynthesized from waste catalyst after oxalic acid leaching and impregnating with various V₂O₅ mass loadings.

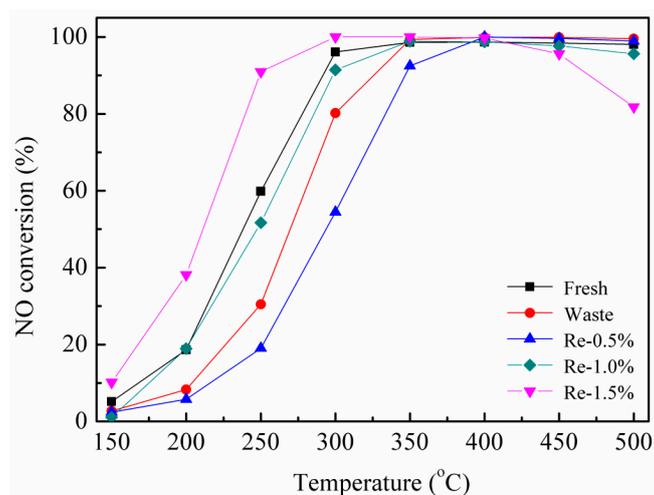


Figure 2. NO conversion of the fresh, waste and resynthesized V₂O₅-WO₃/TiO₂ catalysts prepared from OA leaching residue with different V₂O₅ loadings (Feed: NO = 1000 ppm, NH₃/NO = 1.0, O₂ = 5 vol %. Conditions: total flow rate = 1600 mL/min, gas hourly space velocity (GHSV) = 27,430 h⁻¹).

Among all the catalysts, the resynthesized catalyst loaded with 0.5% V₂O₅ exhibited the poorest activity, even lower than that of the waste catalyst in the temperature range of 150–350 °C. For the resynthesized catalyst containing 1.0% V₂O₅, deNO_x activity was significantly increased and almost recovered to the level of fresh catalyst. The NO conversion was recovered up to 91% at 300 °C. In comparison, the 1.5% V₂O₅-WO₃/TiO₂ catalyst showed even better deNO_x activity at low temperature, with a high NO conversion value of almost 100%, but the conversion decreased markedly at temperature exceeding 400 °C, which was probably caused by the oxidation of NH₃ (2NH₃ + 2O₂ → N₂O + 3H₂O) [8], because the increased N₂O formation with increasing V₂O₅ content was also detected simultaneously. The results revealed that the deNO_x efficiency (both activity and selectivity) of the resynthesized catalysts with different V₂O₅ contents varied considerably, and with V₂O₅ content of 1.0%, the resynthesized catalyst regained a similar activity to the fresh catalyst.

In the real circumstance of NH₃-SCR, SO₂ and H₂O both unavoidably existed in the flue gas, so it is very important for industrial application to investigate the effect of SO₂ and H₂O on the SCR performance of catalysts. In this work, the effects of SO₂ and H₂O on deNO_x activities over fresh, waste and resynthesized 1.0% V₂O₅-WO₃/TiO₂ catalysts were tested, and the results are illustrated in Figure 3. Figure 3a presents the combined effects of SO₂ and H₂O over different catalysts at various temperatures (350, 300 and 250 °C). It can be seen that the NO conversion of fresh, waste, and Re-1.0% catalysts was stabilized during the first 7.5 h run in the absence of SO₂ and H₂O. When 200 ppm SO₂ and 10 vol % H₂O were added into the reaction gas at 350 °C, a slight decline of NO conversion for in the first 0.5 h, and then it nearly stabilized. With the temperature decreasing from 350 to 250 °C,

a more obvious decrease of NO conversion for all catalysts was observed in the coexistence of SO₂ and H₂O. Particularly, sustained declines of NO conversions for fresh, waste, and Re-1.0% catalysts were detected over 8 h at 250 °C, from 43.9% to 33.7%, from 17.6% to 13.0%, and from 43.2% to 42.0%, respectively. This was mainly caused by the easy formation of ammonium bisulfate with increasing NH₃ slip due to the lower NO conversion, and the difficult decomposition of ammonium bisulfate with decreasing temperature [30].

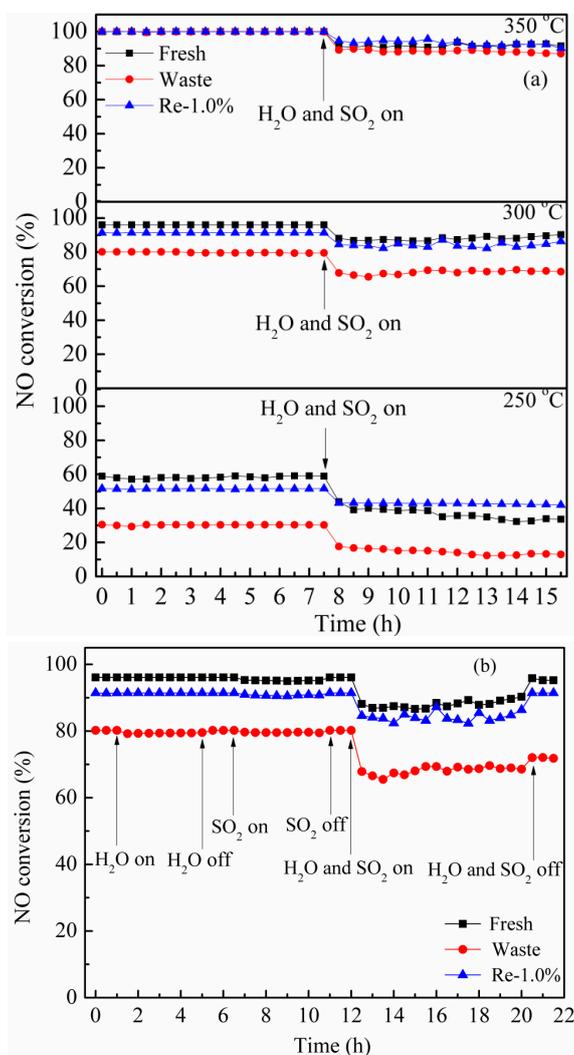


Figure 3. Effects of SO₂ and H₂O on NO conversion over fresh, waste and resynthesized 1.0% V₂O₅-WO₃/TiO₂ catalysts (a) Combined effects of SO₂ and H₂O at 350, 300 and 250 °C; (b) Individual and combined effects of SO₂ and H₂O at 300 °C (Feed: NO = 1000 ppm, NH₃/NO = 1.0, O₂ = 5 vol %, H₂O = 10 vol %, SO₂ = 200 ppm. Conditions: total flow rate = 1600 mL/min, GHSV = 27,430 h⁻¹).

In addition, the individual and combined effects of SO₂ and H₂O over different catalysts were also investigated at a typical temperature (300 °C), as shown in Figure 3b. The individual introduction of 10 vol % H₂O or 200 ppm SO₂ into the reaction gas stream was found to have little effect on the deNO_x activities over all the catalysts. However, when both 200 ppm SO₂ and 10 vol % H₂O were simultaneously added to the reaction gas stream, a significant decrease of NO conversion was found over the fresh and waste catalysts, which was 8% and 12%, respectively during the following 8 h. By contrast, the NO conversion of Re-1.0% catalyst decreased from 91% to 84% at 300 °C, after the introduction of 200 ppm SO₂ and 10 vol % H₂O. After cutting off SO₂ and H₂O, the NO conversion of fresh and Re-1.0% catalyst was almost restored to its original level, and then remained unchanged

during the test period, while the NO conversion over waste catalyst was gradually restored to 72%, which was less than the initial value. The above results suggested that, over the resynthesized 1.0% V₂O₅-WO₃/TiO₂ catalyst, the coexistence of water vapor and sulfur dioxide had a negative effect, but still exhibited a good resistance to H₂O and SO₂ during N reduction by NH₃.

2.3. Textural Properties

The actual V₂O₅ content, specific surface area and VO_x coverage of the abovementioned catalysts are presented in Table 2. The specific surface area of the waste catalyst was similar to that of the fresh catalyst. After OA leaching, the specific surface area of the residue was recovered to 76.9 m²/g owing to the removal of impurities and dissolution of vanadium. It is worth noting that the specific surface area of the resynthesized catalyst decreased to 50.1 m²/g after vanadium impregnation. On one hand, OA leaching would break down the portion of the original microstructure of the catalyst [31]. On the other hand, more vanadium was impregnated into the pores of the TiO₂ carrier, covering the carrier surface, resulting in a decrease of specific surface area.

The calculation of vanadium (VO_x) coverage was based on specific surface area. The deNO_x activity of V₂O₅-WO₃/TiO₂ catalyst is highly dependent on the VO_x coverage on titania, and the monolayer dispersion capacity of vanadia on titania is reported to be 1.14 mmol V/100 m² TiO₂ [32]. Baiker et al. [33] varied the vanadia loading from 0.08 to 0.75 mmol V/100 m² TiO₂ and found that deNO_x activity increased when the vanadia loading increased from 0.18 to 0.3 mmol V/100 m² TiO₂, but decreased with further increases in vanadia loading. From Table 2, the VO_x coverage of the waste catalyst decreased to 0.104 mmol V/100 m² TiO₂, which was considerably lower than that of fresh catalyst (0.139 mmol V/100 m² TiO₂). For the resynthesized catalysts, the VO_x coverage was improved after impregnation of vanadium, and increased significantly with increasing V₂O₅ loadings. In particular, the Re-1.0% catalyst sample had a VO_x coverage of 0.193 mmol V/100 m² TiO₂, which was higher than that of the fresh one, and did not exceed the monolayer dispersion capacity of V₂O₅ on anatase. In addition, the VO_x surface coverage (the fraction of the theoretical monolayer) was also calculated according to the study by Marberger et al. [34]. As listed in Table 2, the waste catalyst had a lower VO_x coverage (15.60%) than the fresh catalyst (20.85%). The resynthesized catalysts showed an increasing surface coverage with increasing V₂O₅ loadings. The surface coverage of the Re-0.5% catalyst sample was 18.30%, which seemed to not have enough active sites for the SCR reaction, and the Re-1.0% catalyst sample had a VO_x coverage of 28.95% and supplied more active sites for the SCR reaction. However, the VO_x coverage of the Re-1.5% catalyst sample increased to 55.95%, and it was reported that the catalyst would have low selectivity when the VO_x coverage was above 50% [34], so the NO conversion of the Re-1.5% catalyst (shown in Figure 2) decreased at temperatures exceeding 400 °C. Therefore, the VO_x coverage of the resynthesized catalysts was improved and the Re-1.0% catalyst sample had an optimized VO_x coverage of 28.95%.

Table 2. V₂O₅ content, specific surface area, and VO_x coverage of the fresh and waste catalysts, OA leaching residue, and resynthesized V₂O₅-WO₃/TiO₂ catalysts.

Catalyst	V ₂ O ₅ Content ^a (wt %)	S _{BET} (m ² /g)	VO _x Coverage	
			mmol V/100 m ² TiO ₂ ^b	% ^c
Fresh	0.71	65.6	0.139	21
Waste	0.53	66.3	0.104	16
OA leaching residue	0.12	76.9	0.017	3
Re-0.5%	0.57	51.5	0.122	18
Re-1.0%	0.98	50.1	0.193	29
Re-1.5%	1.45	43.6	0.373	56

^a Measured by ICP; ^b $\frac{\text{wt \%}/M_{\text{V}_2\text{O}_5} \times 2 \times 1000}{S_{\text{BET}}/100}$, where wt % is the V₂O₅ content, and M_{V₂O₅} is the molecular weight of V₂O₅ [33]; ^c Calculated according to the study by Marberger et al. [34].

2.4. FT-IR Spectra

The FT-IR spectra shown in Figure 4 were investigated to study the supported species arising from V_2O_5 and WO_3 components in the catalysts. The FT-IR spectra were taken with KBr pressed disks exposed to the air and the spectrum of the TiO_2 support has been subtracted. Compared with the fresh catalyst, the waste catalyst showed a broad and strong band at 1122 cm^{-1} , which was assigned to SO_4^{2-} [10,35], and might result from the deposition of sulfates during operation. After OA leaching, the peaks of sulfates on the spectrum were clearly weakened, indicating that the deposited sulfates can be removed, favoring the improvement of catalytic activity of the resynthesized catalysts. Furthermore, the band was shifted from 1122 to 1108 cm^{-1} for the resynthesized catalysts, indicating that the deposited free surface sulfates was changed to bulk sulfates after the resynthesis of catalysts [36]. In addition, the weak band at 1063 cm^{-1} , which showed increased intensity with increasing V_2O_5 content, was associated with the $\nu(S-O)$ stretching of the SO_4^{2-} species interacting with the TiO_2 surface [34]. The broad bands at $988\text{--}993\text{ cm}^{-1}$ were associated with $W=O$ and $V=O$ stretching modes of wolframyl and vanadyl species that are superimposed on each other, and the bands increased slightly in intensity with increasing V_2O_5 content for the resynthesized catalysts [37–39]. The bands in the range of $873\text{--}895\text{ cm}^{-1}$ and the weak broad bands at 942 cm^{-1} were assigned to the $V-O$ stretching mode of the metavanadate species [37,38] and the intensity of both bands decreased slightly with increasing V_2O_5 content for the resynthesized catalysts. This was because with increasing V_2O_5 content, the strongly interacting and stabilized isolated vanadium ions produced by the reaction with surface OH groups of TiO_2 , was gradually transformed into vanadium oxide clusters, more weakly interacting with the TiO_2 surface [37].

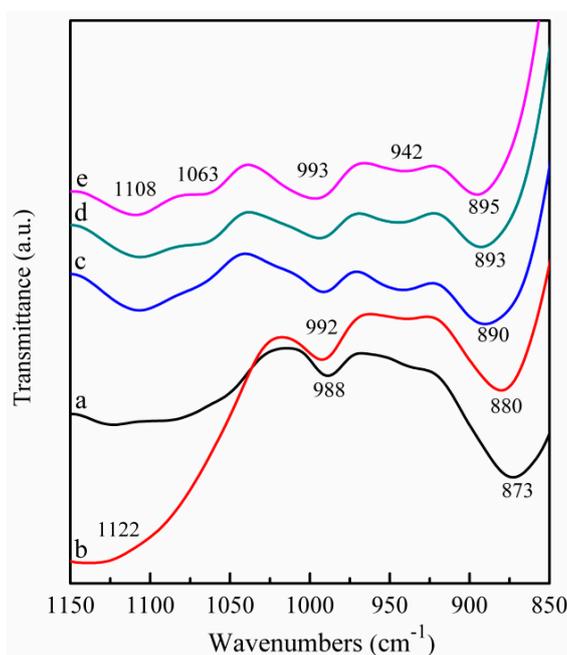


Figure 4. FT-IR spectra for the (a) Fresh (b) Waste (c) Re-0.5% (d) Re-1.0% and (e) Re-1.5% samples after subtraction of TiO_2 support (KBr pressed disk exposed to the laboratory atmosphere).

2.5. XPS Analysis

The V^{4+}/V^{5+} ratio on the SCR catalyst is known to be significantly correlated with $deNO_x$ activity, and a higher V^{4+}/V^{5+} ratio contributed to better $deNO_x$ activity [40,41]. To understand the initial valence states and surface atomic concentration of vanadium, we characterized the catalysts using XPS. The results of V 2p XPS spectra are illustrated in Figure 5.

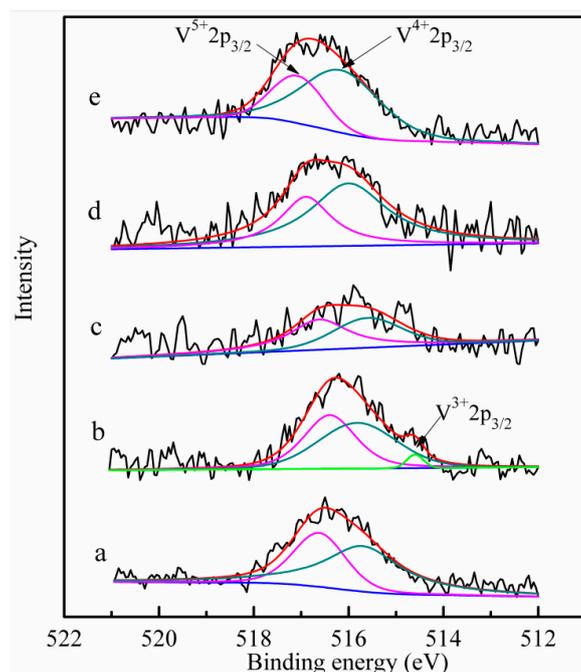


Figure 5. V 2p XPS spectra of the (a) Fresh (b) Waste (c) Re-0.5% (d) Re-1.0% (e) Re-1.5% samples.

According to the V 2p photoelectron peak, V^{5+} is known to appear at 516.4–517.0 eV, V^{4+} at 515.7–516.2 eV [42], and V^{3+} at 513.1–514.7 eV [40], respectively. Clearly, in addition to V^{4+} and V^{5+} , V^{3+} species were observed on the waste catalyst. After leaching, vanadium in the resynthesized catalyst was recovered to exist as V^{4+} and V^{5+} . The concentration ratios of tri-, tetra-, and pentavalent vanadium ions are summarized in Table 3. The concentration of V^{4+} species on the waste catalyst decreased to 51.5% compared with the fresh catalyst (62.5%), and the ratio of V^{4+}/V^{5+} decreased from 1.67 to 1.13. The resynthesis of the catalyst evidently influenced the atomic concentrations, and the V/Ti ratio and the concentration of V^{4+} species on the synthesized catalyst was gradually restored. When the V_2O_5 loading of the resynthesized catalyst increased from 0.5% to 1.5%, the V^{4+}/V^{5+} ratio increased from 0.88 to 2.24. In particular, the concentration of V^{4+} species on the Re-1.0% catalysts sample was restored to 60.8%, and the V^{4+}/V^{5+} ratio was 1.55. Therefore, it can be envisaged that after OA leaching and vanadium impregnating, the ratio of V^{4+} to V^{5+} in the resynthesized catalysts was improved, thus, contributing to the recovery of deNO_x activity.

Table 3. Valence states of V on the fresh, waste, and resynthesized V_2O_5 - WO_3 /TiO₂ catalysts obtained from X-ray photoelectron spectroscopy (XPS) spectra.

Catalyst	Binding Energy (eV)			Surface Atomic Concentration (%)			Surface Atomic Ratio	
	V^{3+}	V^{4+}	V^{5+}	V^{3+}	V^{4+}	V^{5+}	V/Ti	V^{4+}/V^{5+}
Fresh	-	515.7	516.6	-	62.5	37.5	0.046	1.67
Waste	514.6	515.8	516.6	3.0	51.5	45.5	0.036	1.13
Re-0.5%	-	515.7	516.6	-	46.9	53.1	0.037	0.88
Re-1.0%	-	515.9	516.9	-	60.8	39.2	0.047	1.55
Re-1.5%	-	516.1	517.1	-	69.1	30.9	0.076	2.24

2.6. H₂-TPR

It has been established that the oxidative dehydrogenation of the adsorbed ammonia species by vanadia species is a key step in the SCR of NO by NH₃ [43–46]. According to this view, the reduction ability of catalysts was investigated, and the results of H₂-TPR profiles are shown in Figure 6.

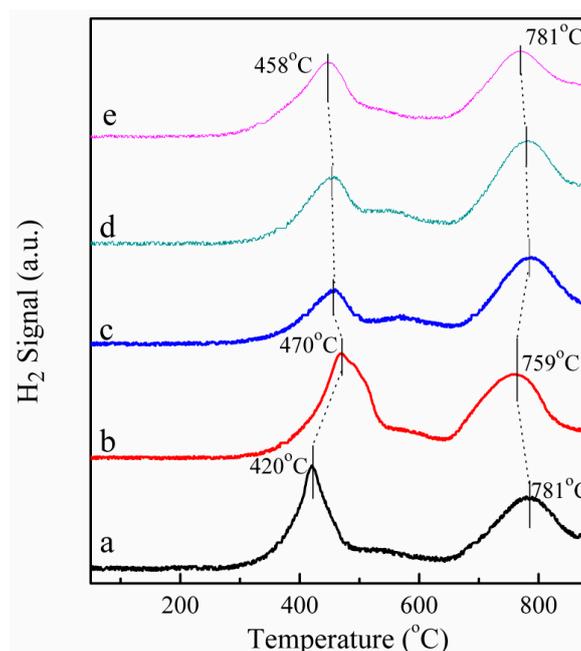


Figure 6. H₂-TPR results of the (a) Fresh (b) Waste (c) Re-0.5% (d) Re-1.0% (e) Re-1.5% samples.

From Figure 6, all catalysts presented two main reduction peaks. The profile of the fresh catalyst showed two reduction peaks located at around 420 and 780 °C, respectively. The first peak was ascribed to the superimposed reduction of $V^{5+} \rightarrow V^{3+}$, $W^{6+} \rightarrow W^{4+}$, and sulfates to SO_2 , and the second peak was attributed to the reduction of $W^{4+} \rightarrow W^0$ [47]. Compared with the fresh catalyst, the reduction peak of V species on the waste catalyst shifted apparently to higher temperature (470 °C), implying the decrease in reduction ability. The main cause was the deposition of alkali metals and alkaline earth metals, which hindered the reducibility of the SCR catalysts and shifted the reduction peak of V species to a higher temperature [48]. Based on this analysis, the decrease of the reducibility should be another reason for the decrease of the activity of the waste catalyst, especially the low-temperature activity.

After OA leaching, the maximum reduction temperature of vanadium decreased to 458 °C, revealing that most of the impurities were removed and that the reducibility of the resynthesized catalysts were partially promoted.

3. Experimental

3.1. Raw Materials and Resynthesis Protocols

The fresh (named Fresh) and waste (named Waste) SCR catalysts used in this work were commercial honeycomb monolith catalysts obtained from Jiangsu Longyuan Catalyst Co., Ltd., Wuxi, China. The catalyst had been used for about 35,000 h with a collapsed honeycomb structure and a dark yellowish gray color.

The waste catalyst was ground and sieved to particles (<100 mesh) and leached by 1.5 mol/L OA ($H_2C_2O_4 \cdot 2H_2O$, Beijing Chemical Works, Beijing, China, 99.5%). Then, the leaching residue was co-impregnated with an aqueous solution of ammonium metavanadate (NH_4VO_3 , Xilong Chemical Co., Ltd., Shantou, China, 99.9%) dissolved in OA. The slurry was standing at 80 °C overnight, dried at 105 °C for 6 h, and subsequently calcined at 600 °C in air for 3 h. The catalysts obtained with a nominal V_2O_5 mass loading amount of 0.5%, 1.0%, and 1.5% were denoted by Re-0.5%, Re-1.0%, and Re-1.5%, respectively.

3.2. Catalytic Activity Test

The catalytic deNO_x activity over all prepared catalysts was evaluated in a fixed quartz reactor (i.d. = 20 mm) operating at atmospheric pressure. The prepared catalysts (50–100 mesh) were loaded into the reactor between quartz wool. A type-K thermocouple was inserted into the catalyst bed to monitor the reaction temperature. The reaction was performed at several temperature levels in the range of 150–500 °C with an interval of 50 °C. The simulated flue gas consisted of 1000 ppm NO, 1000 ppm NH₃, 200 ppm SO₂ (when used), 10 vol % H₂O (when used), and 5 vol % O₂, and the balance gas used was N₂. This reaction stream was fed into the reactor through mass flow controllers with a total flow rate of 1600 mL/min at a GHSV of 27,430 h⁻¹. At each temperature measurement point, all the catalysts were kept on stream for 1 h. Then NO conversion was calculated according to the following equation:

$$\eta_{\text{NO}} = \frac{C_{\text{NO,in}} - C_{\text{NO,out}}}{C_{\text{NO,in}}} \times 100\% \quad (1)$$

where η_{NO} is the NO conversion, $C_{\text{NO,in}}$ and $C_{\text{NO,out}}$ are the NO concentrations in the inlet and outlet gas, as measured by a flue gas analyzer (Lancom 4, Ametek, Bowen, PA, USA), respectively.

3.3. Catalyst Characterization

The chemical compositions of catalysts were determined by inductively coupled plasma atomic emission spectrometer (ICP-AES, Thermo Scientific, Waltham, MA, USA) according to the standard of YS/T 514.9-2009. Each sample was repeated for three times. The XRD patterns of catalysts were obtained by X-ray Diffraction (Empyrean, PANalytical, Almelo, The Netherlands,) by using Cu-K α radiation ($\lambda = 1.54056 \text{ \AA}$, 40 mA and 40 kV) at the scanning range of 5–90 °C. The specific surface area and pore properties of catalysts were determined by N₂ physisorption at –196 °C on an absorption unit (Autosorb-1, Quantachrome, Boynton Beach, FL, USA). Prior to analysis, approximately 0.1–0.2 g samples were evacuated under N₂ atmosphere for 3 h at 300 °C.

FT-IR spectra were recorded in a TENSOR 27 FT-IR apparatus (Bruker, Karlsruhe, Germany). The valence states of elements and surface atomic concentrations in the catalysts were examined by XPS, which was conducted under an ultrahigh vacuum using an ESCALAB 250Xi spectrometer (Thermo Fisher Science, Waltham, MA, USA). Al-K α X-rays were used as excitation light source, with a power of 150 W (15 kV, 10 mA), and the binding energy was corrected with the C 1s peak (284.8 eV).

H₂-TPR was conducted on a chemisorption analyzer (AutoChem II 2920, Micromeritics, Norcross, GA, USA). Prior to analysis, the sample (about 100 mg) was purged in He (50 mL/min) at 300 °C for 60 min, and then cooled to 50 °C. Then the sample was heated from 50 to 900 °C at a rate of 10 °C/min in a mixture of 10% H₂/Ar. The consumption of H₂ was then detected by a thermal conductivity detector (TCD).

4. Conclusions

In this work, the V₂O₅-WO₃/TiO₂ catalysts were synthesized from the waste SCR catalyst after oxalic acid leaching and impregnating with various V₂O₅ mass loadings. The result showed that the deNO_x activity of the newly synthesized catalyst with 1.0% V₂O₅ virtually recovered to the level of fresh catalyst, with NO conversion being recovered to 91% at 300 °C, and it also showed a good SO₂/H₂O resistance. The VO_x coverage for the newly synthesized 1.0% V₂O₅/WO₃/TiO₂ catalyst was optimized to 29% after washing with oxalic acid and impregnation with vanadium, generating more active sites for the SCR reaction. The results of XPS and H₂-TPR analysis demonstrated that the newly synthesized catalyst possessed a higher ratio of V⁴⁺ to V⁵⁺ and a lower reduction temperature of the dispersed V species, compared to the waste catalyst. These results appeared to be beneficial to the recovery of low-temperature deNO_x activity of the resynthesized catalyst.

Supplementary Materials: The following are available online at www.mdpi.com/2073-4344/7/4/110/s1, Figure S1: NO conversion of the fresh, waste catalyst, and waste catalyst loaded with 0.2% V₂O₅.

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