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Nanosized V-Ce Oxides Supported on TiO₂ as a Superior Catalyst for the Selective Catalytic Reduction of NO

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Received: 6 January 2020; Accepted: 3 February 2020; Published: 7 February 2020

Abstract: Nanosized V-Ce oxides supported on TiO₂ (VCT) were prepared and utilized in the low-temperature selective catalytic reduction (SCR) of NO with NH₃. Compared with the other V-Ce oxides-based catalysts supported on Al₂O₃, ZrO₂, and ZSM-5, VCT showed the best SCR activity in a low-temperature range. The NO_x conversion of 90% could be achieved at 220 °C. Characterizations including X-ray diffraction (XRD), scanning electron micrograph (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), temperature-programmed desorption with NH₃ (NH₃-TPD), and temperature-programmed reduction with H₂ (H₂-TPR) showed that V_{1.05}Ce₁/TiO₂ exhibited a good dispersion of V₂O₅, enrichment of surface Ce³⁺ and chemical-absorbed oxygen, and excellent redox capacity and acidity, which resulted in the best SCR performance at low temperature.

Keywords: low temperature SCR; NO_x reduction; V-Ce catalyst

1. Introduction

Nitrogen oxides (NO_x), as one of the main pollutants in the atmosphere, give rise to many environmental problems such as acid rain, photochemical pollution, and haze [1–3]. The selective catalytic reduction (SCR) of NO_x with NH₃ is a relatively mature technique for NO_x abatement from thermal power plants, chemical plants, etc. [4,5], and the deNO_x catalyst is the key factor for the technique [6]. Currently, V₂O₅-WO₃/TiO₂ and V₂O₅-MoO₃/TiO₂ are the most widely used catalysts for NO_x removal because of their high activity and N₂ selectivity [7], but a series of problems still existed, such as the relatively narrow working temperature range of 300–420 °C [8], the high oxidation ratio of SO₂ to SO₃ [5,9], the toxicity of vanadium species [10], and the formation of N₂O at relatively high temperatures [11]. As such, the application of SCR technology in waste incinerators, industrial boilers, as well as biomass fuel power plants has been hindered.

In view of the defects above, much attention has been put into developing efficient SCR catalyst working in low-temperatures or wide range temperatures. Meanwhile, researchers have been working on low vanadium catalysts in recent years, and excellent NO_x conversion has been achieved on supported V₂O₅ catalysts [12–14], but several problems still remain, especially for N₂ selectivity. Since CeO₂ has predominant oxygen storage/release ability and good redox property [15–18], it was

regarded as a critical component of efficient catalysts for SCR. However, pure CeO_2 was rarely used alone as an active component in reaction duo to its poor NH_3 adsorption capacity and high reaction temperature [19]. Nowadays, more and more studies choose CeO_2 as a main modifier or the secondary elements were dropped into CeO_2 to enhance the SCR activity [10,20,21]. Based on the traditional catalysts $\text{V}_2\text{O}_5\text{-WO}_3(\text{MoO}_3)/\text{TiO}_2$, V-Ce mixed oxides-based catalysts such as $\text{V}_2\text{O}_5\text{-CeO}_2/\text{SiO}_2$ [22], $\text{V}_2\text{O}_5\text{-CeO}_2/\text{TiO}_2\text{-ZrO}_2$ [23], and $\text{V}_2\text{O}_5\text{-CeO}_2/\text{WO}_3\text{-TiO}_2$ [24] with high activity at 200–420 °C were developed, and they showed quite different catalytic performances in SCR reaction. However, the detail information including physicochemical properties of V-Ce mixed oxides catalysts over various structures is limited, and the catalytic performance of V-Ce mixed oxides catalysts at low temperatures should be further enhanced.

Generally, the support materials will have an important impact on the performance of SCR catalysts due to the structure/texture and acid/redox properties, the inherent catalytic nature of materials, and the metal-support interaction [25]. Some support materials such as TiO_2 , ZrO_2 , Al_2O_3 , and ZSM-5 can be used for the NH_3 -SCR reaction. Among these oxides, TiO_2 shows a large amount of acid sites on the surface but with low surface areas; ZrO_2 exhibits special characteristics, such as high thermal stability, extreme hardness, and excellent activity at high temperatures, but the activity is poor at low temperatures; $\gamma\text{-Al}_2\text{O}_3$ is a porous solid material with a high specific surface area but shows an obvious inhibition on the SCR reaction in the presence of SO_2 and H_2O [26]; ZSM-5 is porous and shows a high specific surface area but with low acid sites and adsorption capacity.

On the basis of these factors, in this paper, nanosized V-Ce oxides supported on TiO_2 were studied. A series of characterization methods, such as Brunauer-Emmett-Teller (BET) specific surface area and Pore size distributions employing the Barrett-Joyner-Halenda (BJH) model (BET-BJH), scanning electron micrograph (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), temperature-programmed reduction with H_2 (H_2 -TPR) and temperature-programmed desorption with NH_3 (NH_3 -TPD) were conducted to explore the activity of catalysts in SCR reaction, expecting to get the V-Ce catalysts with better catalytic performance and broad application prospect at low temperatures for SCR.

2. Results and Discussion

2.1. Morphology and Structure Investigations

XRD was utilized to determine the bulk crystalline phases in the samples. The XRD results of different catalysts were shown in Figure 1. For the samples of V-Ce oxides supported on TiO_2 (VCT), Al_2O_3 (VCA), ZrO_2 (VCZR) and ZSM-5 (VCZS), most of the strongest peaks in each XRD patterns belonged to their supports, respectively. Among them, the anatase phase (PDF-#21-1272) dominated on VCT and traces of rutile (PDF-#21-1276) phase were also detected, which may resulted from P25 (a precursor of TiO_2) containing about 20% rutile phase. For VCT, VCA, and VCZS, the diffraction peaks of cubic CeO_2 (PDF-#34-0394) were also found, and the diffraction peak of cubic CeO_2 in VCA was much stronger than that in VCT and VCZS, which indicated its high crystallinity. The peak assigned to V_2O_5 was absent in any of the catalysts during XRD analysis, suggesting that V species were highly dispersed and existed in an amorphous state throughout the support structure [27].

The HR-TEM and SEM-EDS mapping results of VCT were plotted in Figure 2. As shown in Figure 2a,b, the lattice fringes of both cubic CeO_2 (111) and (1-1-1) crystal planes with an interplanar spacing of 0.32 nm and 0.31 nm were well-defined in the sample of VCT [28], which was consistent with the observation from XRD results. In addition, the SEM-EDS mapping of Ce, V, Ti, and O elements on the VCT were detected in Figure 2c,d, and it was obvious to notice that all the elements mentioned above were uniformly distributed. Meanwhile, the textural properties of different samples were measured, and the corresponding results were displayed in Table 1. The BET specific surface area of all the catalysts decreased as $\text{VCZS} > \text{VCA} > \text{VCT} > \text{VCZR}$. Among the samples, VCZS exhibited better structure, including the largest BET specific surface area (334.4 m^2/g) but with smaller pore

volume ($0.20 \text{ cm}^3/\text{g}$) while VCT showed lower BET specific surface area ($53.0 \text{ m}^2/\text{g}$) but with higher pore volume ($0.86 \text{ cm}^3/\text{g}$). The largest BET specific surface area of VCZS could mainly attribute to the property of ZSM-5. It was worth noticing that the textural properties of different catalysts did not match with the XRD results, which demonstrated the better morphology of VCT. Even though a larger surface area facilitated the adsorption and activation of reactants during reaction, it may not be the determining factor affecting the catalytic performance in this study. Further correlation between the structural properties and activity would be discussed in the section of catalytic performance.

Figure 1. X-ray diffraction patterns of different samples.

Figure 2. HR-TEM image (a,b) and SEM-EDS mapping images (c,d) of V-Ce oxides supported on TiO_2 (VCT).

Table 1. Textural properties of different samples.

Samples	S_{BET} (m^2/g)	Total Pore Volume (cm^3/g)	Average Pore Diameter (nm)
VCT	53.0	0.86	21.66
VCA	143.1	0.54	16.33
VCZR	5.5	0.03	25.39
VCZS	334.4	0.20	4.51

2.2. Surface Analysis

Figure 3 showed the O 1s XPS spectra of different catalysts. The O 1s peaks could be separated into three peaks: the peaks at lower binding energies (529.3–530 eV) are attributed to the lattice oxygen (hereafter denoted as O_{β}), the peaks at binding energies (530.1–532 eV) are related to the chemical adsorbed oxygen (hereafter denoted as O_{α}), and the peaks at higher binding energies (532.8–533 eV) are related to the hydroxyl oxygen (hereafter denoted as O_{γ}) [29,30]. Chemical adsorbed oxygen always exhibit better catalytic activity than lattice oxygen and hydroxyl oxygen, and it plays an important part in SCR reaction because of its higher mobility. Meanwhile, it can improve the catalytic performance by facilitating the NO oxidation to NO_2 by a fast SCR reaction [31,32]. Thus, the O_{α} ratio, calculated by $O_{\alpha}/(O_{\alpha} + O_{\beta} + O_{\gamma})$, was listed in Table 2 to analyze the catalytic performance of different catalysts. From the results of XPS analysis, VCT and VCA showed similar O_{α} concentration with the $O_{\alpha}/(O_{\alpha} + O_{\beta} + O_{\gamma})$ ratio of 36% and 37%, while VCZR and VCZS were 32% and 5%, respectively. For VCZS, the peak that appeared at 532.8 eV binding energy could be attributed to O_{γ} , which took up 89% of the oxygen state and it mainly came from the ZSM-5 support, while the O_{α} ratio in VCZS was only 5% during the XPS analysis. The higher O_{α} ratio over catalyst was essential for their catalytic performance in SCR reaction. All the differences from four catalysts could be explained by the characteristics of different supports as well as the formation of interaction between active components and supports. Other chemical elements could not be ignored and also tested for further investigation to get comprehensive consideration.

Figure 3. O 1s X-ray photoelectron spectroscopy (XPS) high-resolution scans spectra of different samples.

Table 2. Surface composition of the samples obtained by XPS.

Samples	Atomic Ratio (at.%)		
	$O_{\alpha}/(O_{\alpha} + O_{\beta} + O_{\gamma})$	$Ce^{3+}/(Ce^{3+} + Ce^{4+})$	$V^{4+}/(V^{4+} + V^{5+})$
VCT	36	36	51
VCA	37	29	44
VCZR	32	27	36
VCZS	5	26	36

Figure 4 showed the Ce 3d XPS spectra of different catalysts. The complex spectrum of Ce 3d was decomposed into eight components. These peaks labeled u and v were attributed to the spin-orbit components of the Ce $3d_{3/2}$ and Ce $3d_{5/2}$, respectively. The peaks labeled u''' , u'' , u, v''' , v'' , and v represent the $3d^{10}4f^0$ state of Ce^{4+} , while the bands labeled u' and v' represent the $3d^{10}4f^1$ initial electronic state corresponding to Ce^{3+} [33,34]. The XPS spectra indicated the coexistence of Ce^{3+} and Ce^{4+} species over all the catalysts, and the Ce element mainly existed in the form of CeO_2 . The coexistence of Ce^{4+} and Ce^{3+} was beneficial to the catalytic activity because of its coherent ability

to increase the amount of chemical adsorbed oxygen on the catalyst surface [35]. Table 2 was applied to calculate the surface $\text{Ce}^{3+}/(\text{Ce}^{3+} + \text{Ce}^{4+})$ atomic ratios. Among them, VCT showed the highest $\text{Ce}^{3+}/(\text{Ce}^{3+} + \text{Ce}^{4+})$ atomic ratios of 36%, while VCA, VCZR and VCZS catalysts were calculated at 29%, 27%, and 26%, respectively. As we know, Ce^{3+} came from the ceria defects and was accompanied by the formation of oxygen vacancies; Ce^{3+} and oxygen vacancies can lead to charge imbalance, form an unsaturated chemical bond, promote the adsorption of free oxygen, and enhance the repeatable $\text{Ce}^{4+}/\text{Ce}^{3+}$ redox cycles in the final and thus facilitated the NH_3 -SCR reaction [36]. The promotion effect came from $\text{Ce}^{4+}/\text{Ce}^{3+}$ redox cycles for SCR reaction became more obvious on the VCT sample.

Figure 4. Ce 3d XPS high-resolution scans spectra of different samples.

Figure 5 showed the V 2p XPS spectra of different catalysts. The V 2p peaks could be separated into two peaks: the peaks at binding energies 515.6–516.5 eV and 523.5 eV are attributed to V^{4+} , while the peaks at binding energies 516.8–517.7 eV and 524.8 eV are attributed to V^{5+} [37–39]. The proportions of $\text{V}^{4+}/(\text{V}^{4+} + \text{V}^{5+})$ on different catalysts were calculated, and the results are listed in Table 2. VCT achieved the highest $\text{V}^{4+}/(\text{V}^{4+} + \text{V}^{5+})$ atomic ratios of 51% when compared with that in VCA, VCZS, and VCZR at 44%, 36%, 36%, respectively. It was reported that V^{4+} species in V_2O_5 exist with oxygen defects, while the redox cycles of $\text{V}^{5+}/\text{V}^{4+}$ will be prohibited once the amount of V^{4+} species decreased or disappeared, which will have a negative impact on the redox properties of catalysts [40]. The coexistence of V^{4+} and V^{5+} can generate the unsaturated valence of V to accelerate the adsorption of oxygen and generate active oxygen species. The higher $\text{V}^{4+}/(\text{V}^{4+} + \text{V}^{5+})$ atomic ratios in VCT provided the main active valence state of V^{4+} and it was beneficial for the SCR process.

Figure 5. V 2p XPS high-resolution scans spectra of different samples.

2.3. Reducibility

To investigate the reduction behavior of different catalysts, H_2 -TPR analysis were performed and the results are illustrated in Figure 6. After a peak-fitting deconvolution, the catalysts displayed three peaks at 400–500 °C, 500–600 °C, and 600–720 °C. The first intensity peaks on VCT, VCZS, VCA, and VCZR were observed at 427 °C, 465 °C, 499 °C, and 566 °C, respectively; they belonged to the reduction of CeO_2 on surface and may overlap the reduction peaks of V oxides [41]. It was reported that the lower the reaction peak appeared, the stronger the reducibility was; VCT showed a peak at 427 °C prior to others. The second peaks on VCT, VCZS, and VCA were observed at 500–600 °C, which indicated that various strong interaction between V-Ce mixed oxides on different supports were generated and formed intermediate oxides. The peaks over 600 °C could belong to the reduction of bulk CeO_2 [42], especially for VCZR and VCZS with higher temperature, indicating the difficulty of bulk CeO_2 reduction due to its high crystallinity. Moreover, H_2 consumption was used to analyze the oxygen storage capacity of catalysts, which was a crucial parametric for ceria-based catalysts in SCR reaction [43]. As shown in Figure 6, it was found that H_2 consumption on VCT (542 $\mu\text{mol/g}$) was a little higher than others. The patterns in different shapes of catalysts could be ascribed to effect resulting from the interaction between active components and various supports, which may be the key factors of different catalysts in the improvement of SCR activity at low temperature.

Figure 6. Temperature-programmed reduction with H_2 (H_2 -TPR) profiles of different samples.

2.4. Surface Acidity

The adsorption and activation of NH_3 species on catalyst surface is a key step in NH_3 -SCR reaction, which is greatly affected by the number and strength of the acid sites on the catalyst surface [44]. Therefore, the adsorption behavior of NH_3 on four catalysts was investigated by NH_3 -TPD analysis, as presented in Figure 7. VCZR processed two desorption peaks while VCT, VCA, and VCZS processed three desorption peaks. In terms of VCT, VCA, and VCZS, the peaks “I”, “II”, and “III” were attributed to the NH_3 desorption of weak acid sites, medium acid sites, and strong acid sites [39,45]. For VCZR, the peak attributed to the NH_3 desorption of medium acid sites was absent. It was reported that NH_3 bound to Brønsted acid sites are less thermally stable than the NH_3 molecules bound to Lewis acid sites and could desorb at lower temperatures [46]. In this work, except for VCZR, the peaks “I” and “II” range from 120 to 250 °C at lower temperature and resulted from the NH_3 bound to Brønsted acid sites, while the peaks “III” over 300 °C at higher temperature were ascribed to the NH_3 desorption bound to Lewis acid sites. The peaks on VCZS shifted significantly to higher temperatures than others. To get further discussion, the quantitative analysis of NH_3 -TPD over different samples were also obtained and shown in Table S2. The total amount of adsorbed NH_3 was decreased as follows: VCT (2990) > VCA (2830) > VCZS (2030) > VCZR (1750). VCT showed the higher total amount of adsorbed NH_3 as well as NH_3 adsorption capacity at Brønsted acid sites than others, which may be attributed to their better SCR performance.

Figure 7. Temperature-programmed desorption with NH_3 (NH_3 -TPD) profiles of different samples.

2.5. Catalytic Performance

Figure 8 demonstrated the results of the catalytic performances of nanosized V-Ce based materials for NH_3 -SCR reaction. As shown in Figure 8, NO_x conversion of SCR catalysts at low temperatures decreased in the following order $\text{VCT} > \text{VCZR} > \text{VCA} > \text{VCZS}$, which may be related with the inherent nature of each support and its interaction with V-Ce mixed oxides. It was interesting to find that VCZR exhibited high catalytic activity at 300 °C, but the NO_x conversion started to decrease sharply as soon as the temperature increased over 300 °C. VCA and VCZS all had a wide active temperature window, but their catalytic performances was not obvious at low temperatures and much lower than VCT and VCZR. Compared with others, VCT exhibited the highest SCR activity at the low temperature range of 150–300 °C, over which about 90% NO_x conversion was achieved at 220 °C and a NO_x conversion of 100% at 265 °C could be observed, which showed the best catalytic performance for V-Ce mixed oxides on TiO_2 support at low temperatures. The better catalytic performance on VCT was well matched with the XPS and H_2 -TPR results. Meanwhile, in view of the decrease of NO_x conversion in the order of $\text{VCT} > \text{VCZR} > \text{VCA} > \text{VCZS}$ and combined with the decrease of BET specific surface area in the

order of VCZS > VCA > VCT > VCZR, the results further demonstrated the catalytic performance on catalysts were less related with their structural properties.

Figure 8. Nitrogen oxides (NO_x) conversion with reaction temperature over different samples (Reaction conditions: NO = NH₃ = 700 ppm, O₂ = 3%, balance N₂, 0.5 g catalyst and gas hourly space velocity (GHSV) about 50,000 h^{−1}).

N₂O (a potential by-product of the SCR reaction) was detected and shown in Figure 9. It could be seen that the N₂O concentration of all samples was negligible below 300 °C. When the reaction temperature increased over 300 °C, the N₂O concentration of various catalysts increased with different speed. VCT had better N₂ selectivity with a low N₂O concentration of 50 ppm before 350 °C, while it converted to the fastest growth rate at higher temperatures. Meanwhile, Figure 10 showed the NH₃ oxidation rate of different catalysts and various products, including NO, NO₂, and N₂O, were also tested. Initially, the NH₃ oxidation rate was almost consistent with NO_x conversion and the significant conversion occurred after 250 °C, especially for VCT and VCZR, which was facilitated for the SCR process to promote the reduction of NO_x. Combined with Figure 9, the N₂O concentration over all the catalysts in NH₃ oxidation reaction was consistent with that in SCR reaction before 300 °C, but the N₂O concentration in SCR reaction exceeded that in NH₃ oxidation reaction as the temperature increased over 300 °C. VCT showed poor N₂ selectivity at high temperature, and the increasing N₂O concentration was mainly caused by unselective NH₃ oxidation. Many studies also demonstrated that excessive NH₃ oxidation could decrease the catalytic activity and N₂ selectivity at high temperatures [47].

In short, the catalytic properties of catalysts were influenced by many parameters. By integration of all the factors mentioned above into consideration, the VCT exhibited outstanding catalytic performance at low temperatures. According to TEM and EDS mapping results, nanosized V-Ce oxides supported on TiO₂ led to a good dispersion of all the elements and avoided the aggregation of species on catalysts. Together, it was reported that TiO₂ could promote the formation of active Ce³⁺ species to some extent [38]. In our study, the redox cycles was promoted with higher chemical-absorbed oxygen, Ce³⁺, and V⁴⁺ atomic ratios on the surface of VCT, and this result was consistent with the better catalytic performance on VCT. Furthermore, it was demonstrated H₂-TPR and NH₃-TPD were strongly related with the nature of support oxide, and TiO₂ provided more interaction between active species and support than others, which was mainly represented by a better reduction property and an increased quantity of acid sites. All of above may be contributors to VCT with the highest catalytic performance in SCR reaction.

Figure 9. N_2O concentration with reaction temperature over different samples (reaction conditions: $\text{NO} = \text{NH}_3 = 700$ ppm, $\text{O}_2 = 3\%$, balance N_2 , 0.5 g catalyst, and GHSV about $50,000 \text{ h}^{-1}$).

Figure 10. NH_3 oxidation and concentration profile of NO , N_2O over different samples (reaction conditions: $\text{NH}_3 = 700$ ppm, $\text{O}_2 = 3\%$, balance N_2 , 0.5 g catalyst, and GHSV about $50,000 \text{ h}^{-1}$).

3. Materials and Methods

3.1. Catalyst Preparation

The catalysts were prepared by the wet impregnation method. Ammonium metavanadate and cerium nitrate were used as precursors with a molar ratio of 1.05:1 (V_2O_5 mass ratio of 5% in the catalyst) were completely dissolved in saturated oxalic acid solution and stirred for 3 h to form a mixed solution. Under the agitation, the mixed solution was added into TiO_2 (P25), which dissolved in deionized water. After being dried at 110°C for 12 h, the samples were calcined at 500°C for 3 h. The prepared V-Ce catalyst supported on TiO_2 was named as VCT. For the comparison, V-Ce oxides-based catalysts supported on Al_2O_3 , ZrO_2 , and ZSM-5 were also prepared, and they were named as VCZR, VCA, VCZS, respectively.

3.2. SCR Activity Experiments and Measurement

The NH_3 -SCR activity and N_2O concentration were carried out in a micro catalytic reactor, which consists of a mass flow meter, a reaction gas mixer, and a fixed bed reactor with a 1 cm inner diameter, containing 0.5 g of the catalyst. The reaction conditions were as follows: 700 ppm NO (when used), 700 ppm NH_3 (when used), 1.5% H_2O (when used), 3% O_2 , and N_2 in balance with gas hourly space

velocity (GHSV) of 50,000 h⁻¹ for this system. The concentrations of the reactants and products were measured as follows: inlet and outlet NO_x concentrations were analyzed using a NO_x analyzer (ECOMD, rbr Messtechnik GmbH, Germany), and N₂O concentrations were analyzed using a N₂O analyzer (G200, Geotechnical Instruments Ltd., Coventry, UK).

Independent NH₃ oxidation experiments were also carried out in a micro catalytic reactor, containing 0.5 g of the catalyst. The reaction conditions were as follows: 700 ppm NO, 700 ppm NH₃, 1.5% H₂O (when used), 3% O₂ and N₂ in balance with GHSV of 50,000 h⁻¹ for this system. The concentrations of NH₃ were detected by a FT-IR gas analyzer (Gasmeter DX-4000, Temet Instrument Oy, Helsinki, Finland).

The NO_x conversion in SCR reaction was calculated as:

$$\text{NO}_x \text{ conversion (\%)} = 100\% \times (\text{NO}_{x(\text{in})} - \text{NO}_{x(\text{out})}) / \text{NO}_{x(\text{in})} \quad (1)$$

The NH₃ oxidation rate was calculated as:

$$\text{NH}_3 \text{ oxidation (\%)} = 100\% \times (\text{NO}_{(\text{out})} + \text{NO}_{2(\text{out})} + 2\text{N}_2\text{O}_{(\text{out})}) / \text{NH}_{3(\text{in})} \quad (2)$$

3.3. Catalyst Characterization

The Brunauer-Emmett-Teller (BET) specific surface area (S_{BET}) was determined by a multipoint BET method using the adsorption data in the relative pressure (P/P_0) range from 0.05 to 0.30 and the pore size distributions were calculated by employing the Barrett-Joyner-Halenda (BJH) model on ASAP 2020 (Micromeritics Corporation, Atlanta, GA, USA). The samples were pretreated for 4 h under vacuum conditions at 400 °C to pure the surface before measurements.

The micrograph structures of the samples were observed by scanning electron micrograph on a FEI XL30 ESEM (FEI Inc. Phillips, Hillsboro, Oreg., USA), and the morphology of the samples were detected by transmission electron microscopy (TEM, JEM-2010, JEOL Ltd., Tokyo, Japan) with energies of 200 eV.

X-ray diffraction (XRD) patterns were recorded on an X-ray diffractometer (model D/max RA, Rigaku Corporation, Tokyo, Japan) with Cu K α radiation ($\lambda = 0.15418$ nm), which was used to investigate the crystal phases of the samples and the information was obtained with scattering angles (2θ) ranging from 10° to 80° at a step rate of 10° min⁻¹ with a step size of 0.02.

X-ray photoelectron spectroscopy (XPS) analysis was recorded on ESCALAB 250Xi (Thermo Fisher Scientific, Waltham, USA) with Al K α radiation ($h\nu = 1486.6$ eV, $\lambda = 500$ nm) operated at 150 W to investigate the chemical valence state distribution and the proportions of surface elements. The spectra were recorded in the fixed analyzer transmission mode with energies of 20 eV. The shift of the binding energy due to relative surface charging was corrected using the C 1s level at 284.8 eV as an internal standard. The C 1s high-resolution scans spectra of different samples are shown in Figure S1. Deconvolution was performed with the XPS peak program, and the spectra were decomposed with the least squares fitting routine provided with the software with Gaussian/Lorentzian (80/20) product function and after subtracting the background. Atomic fractions were calculated using peak areas normalized on the basis of sensitivity factors.

Temperature-programmed desorption with NH₃ (NH₃-TPD) and temperature-programmed reduction with H₂ (H₂-TPR) experiments were carried out on a MicroActive for autoChem II 2920 (Micromeritics Corporation, Atlanta, GA, USA). Prior to the NH₃-TPD experiments, samples were purified in He at 200 °C for 1 h and cooled down to 50 °C; then, they were saturated with 5% NH₃/He at room temperature. Desorption was conducted by heating the samples with the heating rate of 10 °C/min from 50 to 800 °C. With respect to H₂-TPR experiments, samples were purified in pure He at 200 °C for 1 h and then cooled to 50 °C. Then, the H₂-TPR experiment was carried out with the linear heating rate of 10 °C/min from 50 to 800 °C in 10% H₂/Ar.

4. Conclusions

In this work, nanosized V-Ce oxides supported on TiO₂ was performed and used for the SCR of NO with NH₃. The V_{1.05}Ce₁/TiO₂ (VCT) catalyst showed the superior catalytic activity at low temperature when compared with VCA, VCZR, and VCZS. The NO_x conversion of 100% could be achieved on VCT at 250 °C. The underlying reasons for catalytic activity between various catalysts were systematically investigated by characterization methods. In the XRD patterns, the anatase phase was the main phase, and the peak assigned to V₂O₅ was absent in VCT, which clearly indicated the strong dispersion of V₂O₅. XPS analysis revealed that VCT was of the higher O_α, Ce³⁺, and V⁴⁺ concentrations, processing higher oxygen mobility and facilitating for the redox process. The NH₃-TPD indicated that VCT had strong adsorption capacity with more surface acid sites. In addition, H₂-TPR showed a reduction peak for VCT at low temperatures, which revealed that the nanosized V-Ce oxides supported on TiO₂ had excellent redox property. In conclusion, all characterization results proved that there was a good dispersion of V₂O₅, and the results may provide useful information for the design of nanosized V-Ce oxides-based catalysts.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2073-4344/10/2/202/s1>, Table S1: The relative atomic ratio of O elements over different samples obtained by XPS, Table S2: Quantitative analysis of NH₃-TPD over different samples, Figure S1(a–d). The C 1s high-resolution scans spectra of different samples.

Author Contributions: Conceptualization, C.H., X.C. and C.C.; Data Curation, L.L.; Investigation, X.W.; Methodology, Y.L.; validation, P.F. and D.C.; writing—original draft preparation, X.W.; writing—review and editing, X.C. and C.C. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Key-Area Research and Development Program of Guangdong Province (2019B110209003), the National Natural Science Foundation of China (41663002), the Natural Science Foundation of Jiangxi Province (20161BAB203080), Jiangxi Institute of Hydraulic Research (20192BAB213027), National Key Research and Development Plan (2016YFC0204101), the Science and Technology Key Projects of Guangdong Province (2017A030223005), the Science and Technology Program of Guangzhou City (201804010147), Pearl River S&T Nova Program of Guangzhou, China (201710010133), and the Central-Level Nonprofit Scientific Institutes for Basic R&D Operations (PM-zx703-201803-077).

Conflicts of Interest: The authors declare no conflict of interest.

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