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Promoting effect of vanadium on catalytic activity of Pt/Ce–Zr–O diesel oxidation catalysts

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ABSTRACT

A series of Pt–V/Ce–Zr–O diesel oxidation catalysts was prepared using the impregnation method. The catalytic activity and sulfur resistance of Pt–V/Ce–Zr–O were investigated in the presence of simulated diesel exhaust. The effect of vanadium on the structure and redox properties of the catalysts was also investigated using the Brunauer–Emmett–Teller method, X-ray diffraction, H₂ temperature-programmed reduction, CO temperature-programmed desorption, X-ray photoelectron spectroscopy, and Energy Dispersive Spectroscopy. Results showed that the Pt particles were well dispersed on the Ce–Zr–O carrier through the vanadium isolation effect, which significantly improved the oxidation activity toward CO and hydrocarbons. An electron-withdrawing phenomenon occurred from V to Pt, resulting in an increase in the metallic nature of platinum, which was beneficial to hydrocarbon molecular activation.

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Introduction

Diesel engines are widely used in vehicles for their high fuel efficiency. As a result, environmental pollution has recently become a serious concern (Zheng et al., 2012; Wiebenga et al., 2012). The control regulations on automobile pollution are being rigorously tightened. To meet these tight regulations, various catalytic exhaust converters are installed to reduce exhaust emissions (Kim et al., 2011; Millet et al., 2009; Christensen and Rak, 2002). In a typical diesel after-treatment system, a diesel oxidation converter (DOC) system is often used in combination with a diesel particulate filtration system and NO_x selective catalytic reduction (SCR) system. The DOC system is popularly used for emission control due to its high oxidation performance (Zhou et al., 2012; Chen et al., 2013), which enhances its capability to oxidize HC and CO to innocuous H₂O and CO₂ (Kamiuchi et al., 2013; Liu et al., 2010). DOC can also

oxidize NO to NO₂, which is beneficial for rapid SCR reaction and particle oxidation in the downstream (Tronconi et al., 2007; Colombo et al., 2012). Pt-based diesel oxidation catalysts are widely used in DOC systems. However, Pt-based catalysts are expensive and easily poisoned by SO₂ in diesel exhaust (Xie et al., 2006; Corro et al., 2003; Dawody et al., 2005; Lu et al., 2008; Yoshimura et al., 2007; Zhu et al., 2013; Yang et al., 2013; Sharma et al., 2013). Moreover, activity at low temperatures also is critical for a diesel oxidation catalyst because the temperature of diesel exhaust gas is significantly lower than that of gasoline exhaust.

Other noble metals are often used to modify Pt metal to improve its catalytic performance and sulfur resistance. For example, Morlang et al. (2005) found that the light-off temperature of CO and HC oxidation could be decreased by the function of synergetic effect of Pt and Pd. Beck and Sommers (1995) investigated the effect of sulfur on a Pt-based

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three-way catalyst, and the result revealed that Pt–Rh showed excellent C_3H_6 low-temperature activity and that the effect of SO_2 on the activity could be completely reversible. Liu et al. (2013) prepared a three-dimensional Pt–Au/CeO₂ catalyst and discovered that the formation of a Pt–Au alloy and its interaction with CeO₂ are mainly responsible for the improvement in catalytic performance for CO oxidation. In addition, Pt-based catalysts modified by two different metals were also investigated in many studies, such as Pt–Pd–Ru/C catalysts (Arikan et al., 2013) and Pt–Ag–Au nanoparticles (Zhang et al., 2011). However, precious metal resources are limited, and large-scale industrial application could be extremely expensive. Therefore, doping non-noble metals into Pt-based catalysts is a possible alternative.

Wu et al. (2012) reported that adding WO_x to Pt/Al₂O₃ (Pt/WO_x/Al₂O₃) can improve its behavior in C_3H_8 oxidation compared with Pt/Al₂O₃ alone. Kim et al. (2011) tried Fe doping on Pt/Al₂O₃, and the result showed that the sulfur resistance of the catalyst evidently increased. Zheng et al. (2013) investigated the effect on the conversion of C_3H_8 after loading Ni on the diesel oxidation catalyst Pt/Ce_{0.4}Zr_{0.6}O₂, and the result suggested that catalytic activity was enhanced because of the strong interaction between Ni and Pt. However, the exhaust temperature of the diesel engine is significantly lower than that of gasoline, particularly in the start-up region. Thus, developing catalytic activity at low temperature is critical for diesel oxidation catalysts. V-based catalysts that achieve excellent sulfur resistance are commonly used in the SCR reaction in the form of composite oxides, such as V₂O₅–WO₃/TiO₂ (Yang et al., 2012) and V₂O₅–CeO₂/TiO₂ (Huang et al., 2008). Vanadium is also used as an additive to modify the carriers to control SO_2 poisoning. Kim et al. (2003) prepared Pt/TiO₂ diesel oxidation catalysts, and after loading V₂O₅ on TiO₂, they found that V₂O₅ could inhibit the oxidation of SO_2 to SO_3 and could also suppress the adsorption of SO_2 on the support. More importantly, vanadium oxide is a superior material in terms of providing oxygen, which is important in an oxidation reaction. In recent studies, the use of vanadium as active ingredient to modify the catalytic performance of catalysts has only rarely been reported. Thus, whether vanadium could accelerate the catalytic activity in a low-temperature region when impregnated along with platinum is an interesting and promising topic.

In this study, a series of Pt–V/Ce–Zr–O diesel oxidation catalysts with different Pt/V ratios were prepared using the impregnation method. The effect of V on catalytic activity and sulfur resistance was investigated in detail. In addition, several analytical techniques, including Brunauer–Emmett–Teller (BET) analysis, X-ray diffraction (XRD), H₂ temperature-programmed reduction (H₂-TPR), CO temperature-programmed desorption (CO-TPD), X-ray photoelectron spectroscopy (XPS), and Energy Dispersive Spectroscopy (EDS) were used to evaluate the effect of V on catalytic behavior. According to the results, the Pt–V/Ce–Zr–O with only 1 wt.% Pt catalyst showed the highest catalytic performance with V loading of 1 wt.%, and its catalytic activity and sulfur resistance were better than those of the 2Pt/Ce–Zr–O with only 1 wt.% Pt. The mechanism of the interaction between vanadium and platinum in the reaction was also explored.

1. Experimental

1.1. Catalyst preparation

The Ce–Zr–O support with cerium to zirconium mol ratio of 4:1 was prepared by co-precipitation. Ce(NO₃)₃·6H₂O and Zr(NO₃)₄·3H₂O were dissolved together in deionized water to form a solution. Oxalic acid was also dissolved using deionized water in another beaker (the oxalic acid amount was twice the total Ce–Zr metal content in terms of mol ratio). The oxalic acid solution was slowly added while stirring via a peristaltic pump to an excess of Ce–Zr–O solution. The precipitate was centrifuged, washed, dried at 110°C, and calcined at 600°C for 3 hr. Pt–V/Ce–Zr–O catalysts with different Pt/V ratios were prepared using the incipient wetness impregnation method, in which H₂PtCl₆ and NH₄VO₃ solutions were used as Pt/V precursors. Pt and V species were loaded by co-impregnation. The catalysts were labeled as xPt–yV/Ce–Zr, where, x and y respectively represent the mass percentage of platinum and vanadium over the support. The prepared solutions were impregnated uniformly by slow removal of water using a rotary evaporator for approximately 60 min at 70°C. The catalysts were then dried at 110°C and calcined at 600°C for 3 hr. A heating ramp rate of 5°C/min was used to reach the final temperature. Finally, 1Pt/Ce–Zr, 1Pt–0.5 V/Ce–Zr, 1Pt–1V/Ce–Zr, 1Pt–2V/Ce–Zr, 1Pt–3V/Ce–Zr, and 2Pt/Ce–Zr were obtained.

1.2. Catalytic activity measurement

The evaluation of catalyst activity was conducted using a fixed-bed continuous reactor packed with 0.5 g catalyst and 1.5 g quartz sand. HC, CO, and NO oxidations were conducted in a stream of simulated diesel exhaust. The feed (CO 1000 ppm, NO 500 ppm, C_3H_6 500 ppm, O₂ 10%, and N₂ balance) was introduced to the catalyst at a flow rate of 200 mL/min (gas hourly space velocity (GHSV) = 24,000 mL/(hr·g cat.)). For SO_2 poisoning, the catalysts were fed with SO_2 (200 ppm in N₂) at 240°C for 5 hr. The effluent gas was analyzed using an online Fourier transform infrared spectrophotometer (VERTEX70, Bruker, Germany) equipped with a multiple reflection transmission cell (Infrared Analysis Inc., path length 10.0 m). All spectra were taken at a resolution of 2.5 cm^{–1} for 32 scans. The curve for the relationship between conversion and temperature was obtained in the light-off experiment. The temperature was programmed from 120 to 330°C under simulated conditions. The concentrations of C_3H_6 , CO, and NO were measured every 30°C. Each temperature was maintained for 60 min.

1.3. Characterization

The specific surface areas of catalysts were measured using the BET method from the nitrogen adsorption isotherms. The experiments were conducted on a ASAP 2020 instrument (Micromeritics) at 77 K. Prior to the experiments, samples were degassed at 473 K for 4 hr.

XRD data on the samples were collected using a SCINTAG XTRA X-ray diffractometer (Shimadzu) equipped with Ni-filtered Cu K α (λ = 1.542 Å, 40 kV) radiation. The measurements were

conducted in the 2θ range of 10 to 90° with a step size of 0.033°.

H₂-TPR experiments were performed on a Autochem 3010E instrument (Zhejiang Fine-tech instruments, China). A desired amount of the samples (100 mg) was placed in a quartz reactor, pretreated under a flow of Ar gas at 200°C for 2 hr, and cooled to 50°C. A gas mixture of H₂ (5%)–Ar (95%) was then passed (30 mL/min) through the reactor. The temperature was increased from 50 to 900°C at a heating rate of 10°C/min. A TCD detector was employed at the outlet of the reactor to measure the volume of hydrogen consumed during reduction.

CO-TPD experiments were performed on a Autochem 3010E instrument (Zhejiang Fine-Tech instruments, China). A desired amount of the samples (100 mg) was placed in a quartz reactor, pretreated in a flow of He gas at 200°C for 2 hr, and cooled to 30°C. A gas mixture of CO (5%)–N₂ (95%) was passed (30 mL/min) through the reactor for 1 h, after which a flow of He was passed (30 mL/min) through the reactor for 1 hr. The temperature was increased from 30 to 500°C at a heating rate of 5°C/min. A TCD detector was employed at the outlet of the reactor to measure the volume of CO during desorption.

Photoelectron spectroscopy was carried out with a spectrometer from Kratos AXIS Ultra DLD with a monochromatized microfocused Al X-ray source. Charging of samples was corrected by setting the binding energy of adventitious carbon (C1s) to 284.6 eV. Prior to the measurements, the powder samples, pressed into self-supporting disks, were loaded into a sub-chamber and then evacuated at 25°C for 4 hr.

2. Results and discussion

2.1. Catalytic activity and sulfur resistance

The conversion of C₃H₆, CO, and NO in the presence of simulated diesel exhaust is shown in Fig. 1. The 1Pt/Ce–Zr catalyst without any vanadium doping exhibited the lowest activity from 180 to 330°C, and the “light-off” temperature reached 230 and 220°C during C₃H₆ and CO oxidation, respectively. After loading with vanadium, a significant promotional effect was noted from 180 to 330°C for C₃H₆ and CO oxidation. In addition, more than 90% C₃H₆ and CO conversion was achieved at nearly 240°C for the 1Pt–1V/Ce–Zr catalyst. However, the further loading of vanadium would cause a decrease in conversion for both C₃H₆ and CO oxidation. From Fig. 1c, we can observe a slight difference in NO oxidation compared with C₃H₆ and CO oxidation. This reveals that the conversion of NO changes slowly over the 1Pt/Ce–Zr catalyst before 240°C because NO oxidation in the low-temperature region is mainly achieved by self-oxidation without the help of a catalyst (Liu, 2011). Moreover, after doping with vanadium, catalytic activity was promoted. The 1Pt–1V/Ce–Zr catalyst could even achieve nearly 75% NO conversion around 240°C, which is beneficial for the subsequent SCR reaction. To evaluate the sulfur-poisoning resistance of the catalysts, the effect of SO₂ on C₃H₆, CO, and NO conversion was investigated. The results are displayed in Fig. 2. We find that 200 ppm SO₂ had a distinct poisoning effect on C₃H₆ and CO conversion over the 1Pt/Ce–Zr sample from 180 to 330°C. However, after loading with

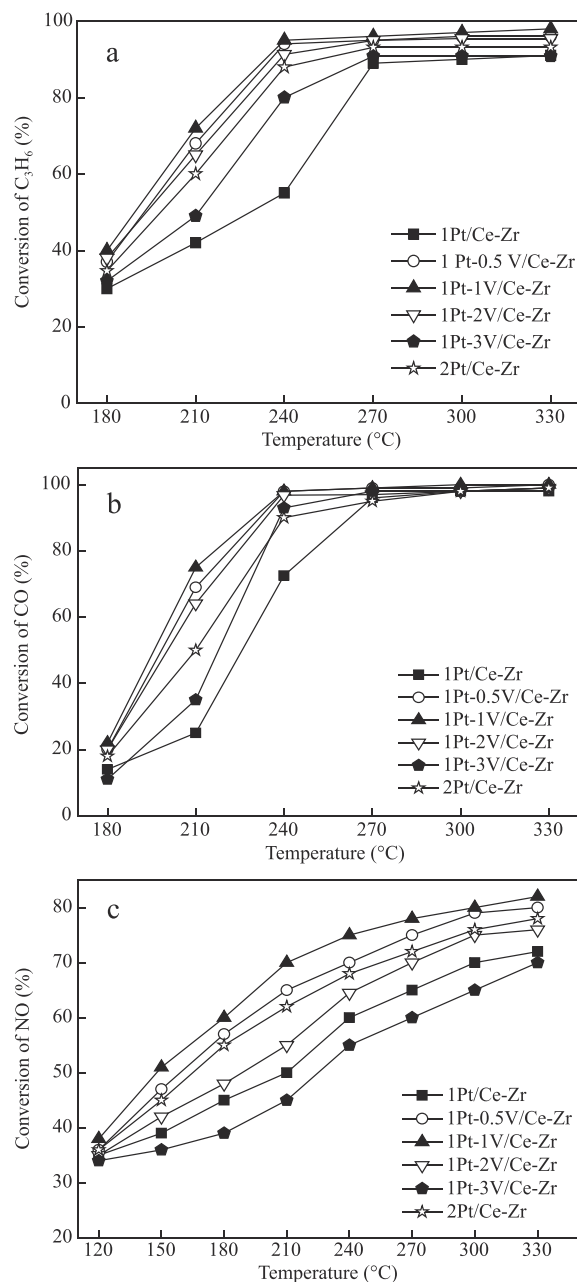


Fig. 1 – Conversion of C₃H₆ (a), CO (b), and NO (c) over Pt–V/Ce–Zr catalysts in a stream of simulated diesel exhaust without SO₂. Conditions: CO 1000 ppm; NO 500 ppm; C₃H₆ 500 ppm; O₂ 10% with N₂ balance, GHSV 24,000 mL/(hr·g cat.).

vanadium, only a slight decline in C₃H₆ and CO conversion was observed when 200 ppm SO₂ was added to the reaction gas, and the 1Pt–1V/Ce–Zr sample could reach 90% C₃H₆ and CO conversion at approximately 240°C. Fig. 3 summarizes the effect of V content on light-off temperature (T_{50}) for C₃H₆ and CO oxidation in the presence of 200 ppm SO₂ and after SO₂ poisoning for 5 hr. The behavior could be correlated well with the above discussion in terms of the T_{50} of C₃H₆ and CO oxidation over the 1Pt–1V/Ce–Zr catalyst, which had the smallest decrease when treated with SO₂ under various conditions. This indicates that the catalyst has strong

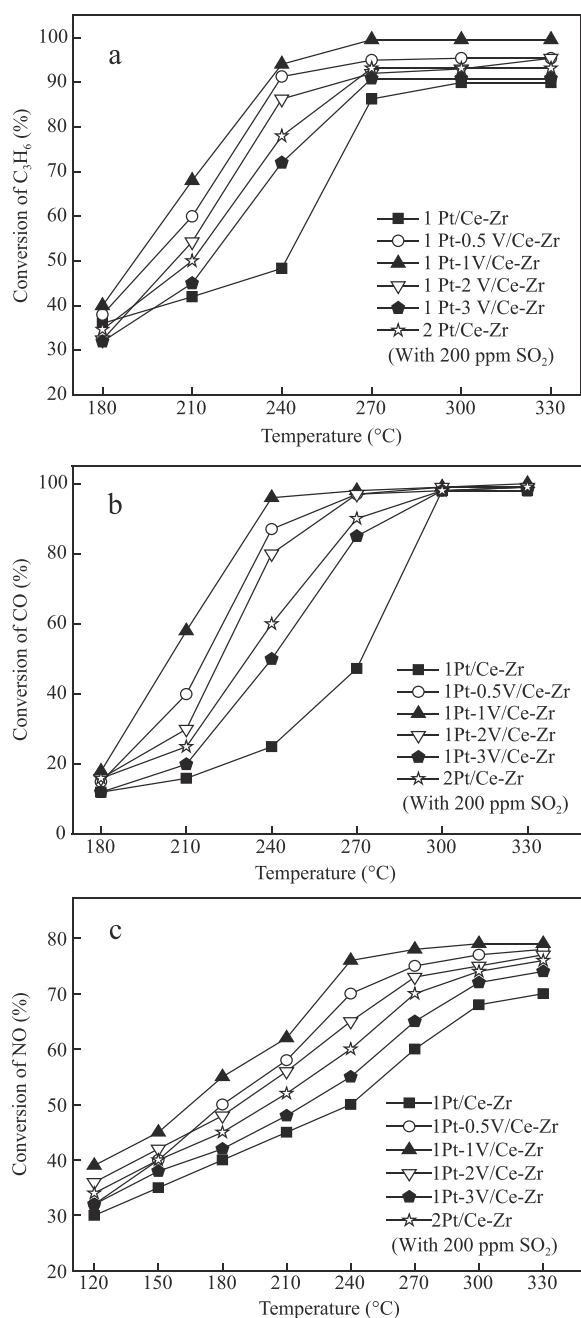


Fig. 2 – Conversion of C_3H_6 (a), CO (b), and NO (c) over Pt-V/Ce-Zr catalysts in a stream of simulated diesel exhaust with 200 ppm SO_2 . Conditions are the same as Fig. 1.

resistance against sulfur poisoning after loading with an appropriate amount of vanadium. From Fig. 2c, we find that the effect of SO_2 on NO catalytic oxidation is not as evident as that for C_3H_6 and CO oxidation. This condition may be attributed to the effect of SO_2 on NO oxidation being mainly in the low-temperature region, whereas the reaction between NO and O_2 dominates this process.

From the above results, we can conclude that the 1Pt-1V/Ce-Zr catalyst shows the highest performance, which is even better than that of the 2Pt/Ce-Zr catalyst. Therefore, the 1Pt-1V/Ce-Zr sample was selected for further

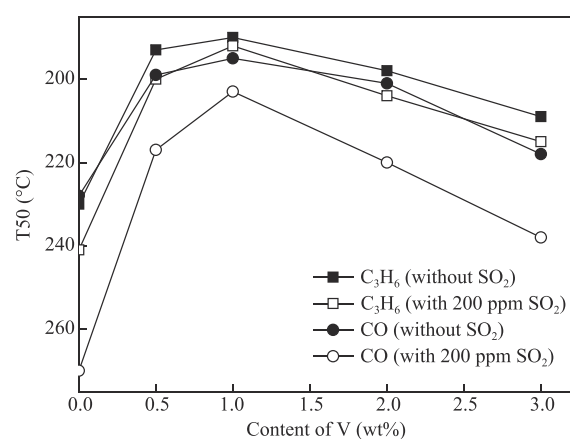


Fig. 3 – Effect of V content on the light-off temperature (T_{50}) of Pt-V/Ce-Zr catalysts in simulated diesel exhaust with or without SO_2 .

investigation in subsequent measurements. To evaluate the effect of vanadium doping on the stability of the catalyst, 1Pt/Ce-Zr and 1Pt-1V/Ce-Zr samples were subjected to a continuous flow of 200 ppm SO_2 at 240°C for 20 hr. The results are shown in Fig. 4. The conversion of C_3H_6 and CO slightly declined after 5 hr for the 1Pt/Ce-Zr single catalyst, but for the 1Pt-1V/Ce-Zr catalyst, the conversion of C_3H_6 , CO, and NO remained stable during the whole simulated process. This reveals that loading with an appropriate amount vanadium can not only improve the catalytic performance and cause a decrease in the amount of noble metal Pt required, but also enable excellent stability in actual operation conditions.

2.2. Catalyst characterization

2.2.1. Structural and textural characterization

An X-ray powder diffraction experiment was conducted to investigate the effect of vanadium loading on structure evolution. Fig. 5 shows that all samples display the pattern of CeO_2 , and no Pt phase is observed, probably because Pt is quite homogeneously distributed on the surface of the support. A minimal amount of V_2O_5 phase was observed when loading with 3 wt.% V, which is possibly attributed to vanadium oxide species aggregating on the surface of the support when vanadium loading is higher than its dispersion threshold (Xu et al., 2002). The lattice constants and mean crystallite sizes of CeO_2 in all samples were calculated using the Bragg law and Scherrer equation, respectively. The results are shown in Table 1. The lattice constants show no change compared with that of pure CeO_2 , the lattice constant of which is 0.5403 nm, and the mean crystallite size is 17 nm. This finding indicates that platinum and vanadium exist on the surface of the support without entering into the structure of CeO_2 . The BET surface decreases with increasing total Pt-V loading because the sintering phenomenon becomes serious when loading with more metals (Kamiuchi et al., 2013). The BET surface of the 1Pt-1V/Ce-Zr sample is 31 m^2/g , which is slightly larger than that of the 2Pt/Ce-Zr catalyst with a

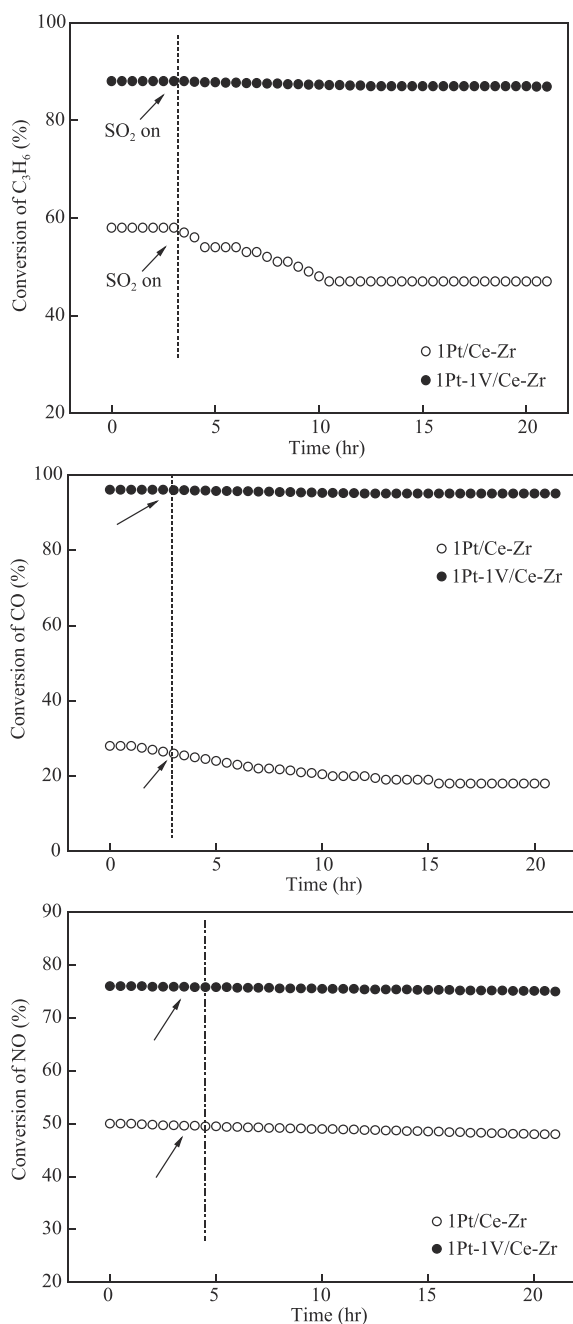


Fig. 4 – Stability of 1Pt/Ce-Zr, 1Pt-1V/Ce-Zr fresh catalyst in simulated diesel exhaust with 200 ppm SO₂ under 240°C for 20 hr.

BET surface area of 25.3 m²/g. It shows that modification of Pt-based catalysts by vanadium can increase the BET surface area.

2.2.2. H₂-TPR characterization

The effect of vanadium loading on redox properties of catalysts investigated by H₂-TPR experiments is illustrated in Fig. 6. The pure Ce-Zr-O support shows two reduction peaks at 500 and 780°C, which can be assigned to the reduction of surface oxygen and bulk oxygen of the support, respectively. The special orbital configuration of precious metals can

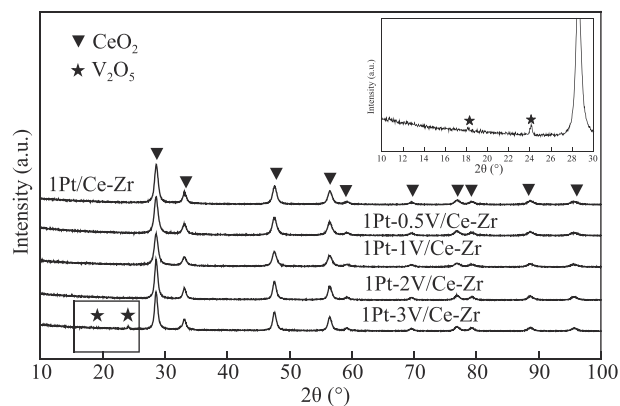


Fig. 5 – XRD (X-ray diffraction) patterns of Pt-V/Ce-Zr catalysts with different vanadium loadings.

significantly enhance the capability of electron transfer in the process of redox, which decreases the reduction temperature of surface oxygen on the support (Zhong et al., 2011). The reduction temperature decreases to nearly 230°C with 1 wt.% platinum loading. Surprisingly, the reduction temperature of surface oxygen continued to decrease with vanadium loading, and the temperature approached 185°C when loaded with 1 wt.% V. However, the reduction temperature of surface oxygen began to increase with further increases in vanadium loading, which is consistent with the behavior of catalytic activity mentioned above. The H₂ consumption of all catalysts calculated by integrating the corresponding peak areas compared with a standard sample (CuO) is shown in Table 1. A positive correlation was found in that the variation of the amount of consumed H₂ is related to the change in reduction temperature and catalytic activity. This reveals that the 1Pt-1V/Ce-Zr sample that achieved the best catalytic behavior had the largest H₂ consumption (the amount of consumed H₂ was 510 μmol/g). According to the literature (Wang et al., 2013), the dispersion of active ingredients on the surface of the catalyst significantly affects the reduction of surface oxygen. H₂ could be more easily activated with higher dispersion of Pt, resulting in an increase in H₂ consumption. Thus, we can suppose that the dispersion of Pt gradually increases with vanadium loading, which enhances the redox capability over the catalysts. The 1 wt.% vanadium loading produces the optimum dispersion, because the presence of excessive vanadium will cover the Pt sites.

2.2.3. CO-TPD characterization

Fig. 7 shows the effect of adding vanadium on the dispersion of Pt, which is measured by the CO-TPD method. The desorption of CO from precious metal (Pt) requires a certain temperature because CO adsorption over Pt can be classified as chemisorption (Hauff et al., 2010). Thus, we can estimate the extent of Pt dispersion based on the amount of CO desorption from the catalysts. Three catalysts with different vanadium loadings (1Pt/Ce-Zr, 1Pt-1V/Ce-Zr, and 1Pt-3V/Ce-Zr) were tested to study the effect of vanadium loading upon Pt dispersion. The results reveal that adsorption of CO for the catalyst with 1 wt.% V loading is 1.5 times that of the 1Pt/Ce-Zr

Table 1 – Surface area, hydrogen consumption, X-ray photoelectron spectroscopy and Energy Dispersive Spectroscopy results and properties of catalysts.

Samples	2θ	Lattice constant (nm)	Crystallite size (nm)	BET surface (m ² /g)	Pt (wt.% EDS)	H ₂ consumption (μmol/g)	Binding energy (eV)		O _β /O _{total} (%)
							Pt4f _{7/2}	V2P _{3/2}	
1Pt/Ce–Zr	28.6279	0.5396	17.3	34.1	2.67	450	73.3	/	14.46
1Pt–0.5V/Ce–Zr	28.6204	0.5398	17.1	33.2	/	480	/	/	/
1Pt–1V/Ce–Zr	28.4653	0.5427	16.1	31.0	3.68	510	73	517.6	16.83
1Pt–2V/Ce–Zr	28.5452	0.5412	16.5	22.1	/	470	/	/	/
1Pt–3V/Ce–Zr	28.5130	0.5418	16.6	20.3	2.43	420	/	/	/
2Pt/Ce–Zr	/	/	/	25.3	/	/	/	/	/

"/" means that the data were not determined.

catalyst. This observation indicates that active Pt sites over the 1Pt–1V/Ce–Zr sample outnumber those over the 1Pt/Ce–Zr catalyst with no vanadium. That is, the dispersion of Pt for the 1Pt–1V/Ce–Zr sample is higher than that of the 1Pt/Ce–Zr catalyst.

However, further addition of vanadium causes a decrease in Pt dispersion because excessive vanadium covers the active Pt sites, such that an evident decline in catalytic activity is observed. We also find the same tendency from the result of EDS and transmission electron microscopy (TEM, shown in Fig. 8). Table 1 shows the surface content of Pt for 1Pt/Ce–Zr, 1Pt–1V/Ce–Zr, and 1Pt–3V/Ce–Zr samples. These three catalysts achieve a mass percentage of Pt of 2.67%, 3.68%, and 2.43% over the surface of the support, respectively (see Table 1). We can conclude that the dispersion of Pt gradually increases with vanadium loading, and 1 wt.% V loading achieves the optimum dispersion, because the presence of excessive vanadium covers the Pt sites. Thus, appropriate vanadium loading is helpful to obtain higher Pt dispersion, which is important for the catalytic activity of catalysts.

2.2.4. XPS characterization

The Pt4f and O1s XPS spectra of 1Pt/Ce–Zr, 1Pt–1V/Ce–Zr samples are presented in Fig. 9a and b, and the relevant data are summarized in Table 1. The Pt4f XPS spectra have two

peaks, as determined by its nature. The binding energy of Pt4f_{7/2} for the 1Pt/Ce–Zr catalyst is 73.3 eV, which indicates that Pt exists in the +2 state. This result is similar to the research by Kim et al. (2003). After loading with 1 wt.% V, the binding energy of Pt4f_{7/2} declines to 72.0 eV. This observation reveals that adding an appropriate amount of vanadium could decrease the oxidation state of Pt, such that the metallic nature of Pt is enhanced. According to the literature (Hu et al., 2012) we can conclude that an electronic interaction occurs between platinum and vanadium. Given that the electronegativity of Pt (2.22) is higher than that of V (1.63), vanadium will donate electrons to platinum, and vanadium species will be oxidized, thus providing the oxygen for CO and NO oxidation (Zhou et al., 2012; Hu et al., 2012). Meanwhile, the lower oxidation state of Pt gives it a more metallic nature, which serves a key function in activating hydrocarbons. Thus, the catalytic activity of the catalyst is promoted.

The O1s XPS spectra can be resolved into two peaks: surface lattice oxygen (O_α) at 529 to 530 eV and surface-adsorbed oxygen (O_β) at 530 to 532 eV. From the calculated percentage of O_β/O in Table 1, the O_β concentration of the 1Pt–1V/Ce–Zr sample as a percentage of total oxygen species (16.83%) is higher than that of the 1Pt/Ce–Zr sample (14.46%). The surface-adsorbed oxygen of the catalyst is the most active oxygen in redox reactions, and an increase in this oxygen is

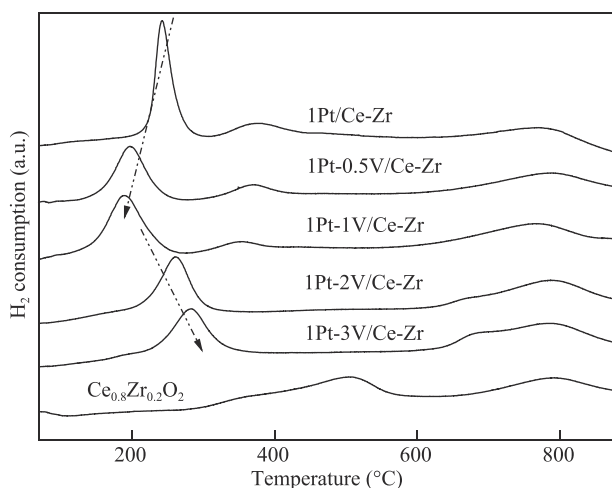


Fig. 6 – H₂-TPR (H₂-temperature-programmed reduction) profiles of Pt–V/Ce–Zr catalysts with different vanadium loadings.

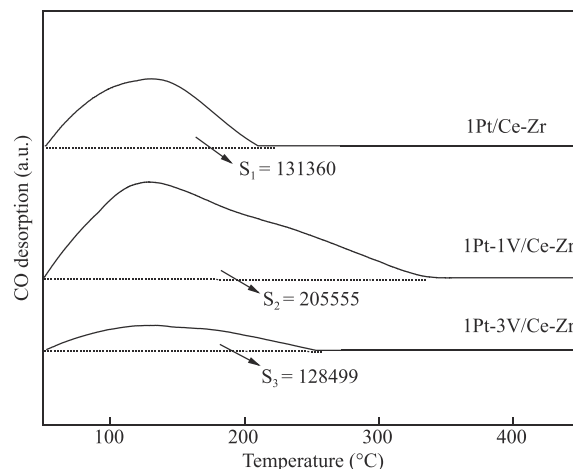


Fig. 7 – CO-TPD (CO temperature-programmed desorption) profiles of 1Pt/Ce–Zr, 1Pt–1V/Ce–Zr, 1Pt–3V/Ce–Zr catalysts.

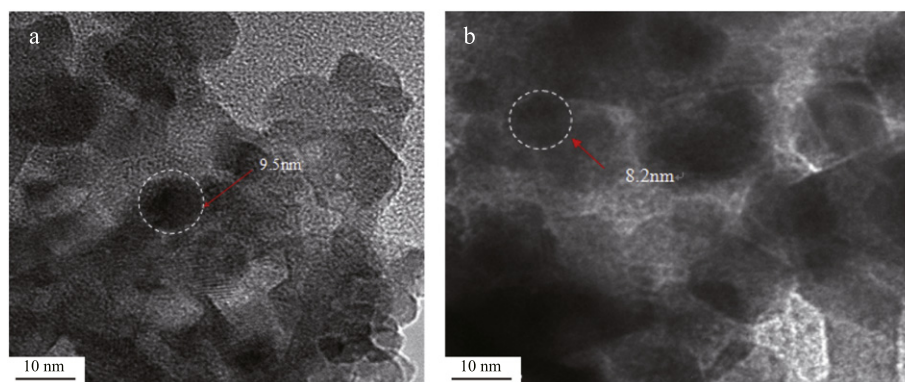


Fig. 8 – TEM (Transmission Electron Microscope) images of (a) 1Pt/Ce-Zr, (b) 1Pt-1V/Ce-Zr catalysts.

beneficial for oxidation efficiency. However, in Fig. 9b, the binding energy of surface lattice oxygen (O_a) is also reduced after loading with 1 wt.% V, which implies that the surface lattice oxygen is increased. This condition may have been caused by V_2O_5 species distributed uniformly on the support, serving as a bearer for providing oxygen. In sum, the total oxygen over the catalyst is enhanced by loading an appropriate amount of vanadium.

In summary, the dispersion and oxidation states of Pt are directly associated with the catalytic activity. The Pt atoms reunite on the 1Pt/Ce-Zr sample, which would lead to the increase of Pt particles, thus causing a decrease in the active Pt sites exposed on support. Moreover, a large amount of oxygen would be adsorbed onto the Pt surface during oxidation, such that platinum would be oxidized by the adsorbed oxygen. The capability to activate hydrocarbons would be weakened by the high oxidation state of Pt. Moreover, when polluted with SO_2 , SO_2 will adsorb on the surface of the support, causing the catalyst to become poisoned.

After loading with an appropriate amount of vanadium, Pt dispersion increases because vanadium is distributed evenly among the Pt particles. Moreover, the vanadium donates electrons to platinum because the electronegativity of platinum is higher than that of vanadium. Thus, more oxygen will be adsorbed on the surface of vanadium, the oxidation state of

Pt will decrease, and the metallic nature of Pt will be enhanced accordingly. Meanwhile, VO_x species provide oxygen for CO and NO oxidation. Moreover, the SO_2 tends to adsorb on vanadium species, which can inhibit SO_2 poisoning of platinum, which is the reason why sulfur resistance develops. However, excessive vanadium loading will cover the active Pt sites, such that an evident decline in catalytic activity will be observed.

3. Conclusions

The catalytic activity and sulfur resistance of catalysts were both improved after loading with an appropriate amount of vanadium. Moreover, 1 wt.% V loading achieved the best catalytic performance. The dispersion of Pt is improved by loading an appropriate amount of vanadium, but excessive vanadium will cover the active Pt sites. Moreover, results reveal that adding an appropriate amount of vanadium could cause a decrease in the oxidation state of Pt, such that the capability for activating hydrocarbons is enhanced, and can inhibit SO_2 poisoning of platinum. Most importantly, the amount of the noble metal Pt can be reduced when Pt is modified with an appropriate amount of V.

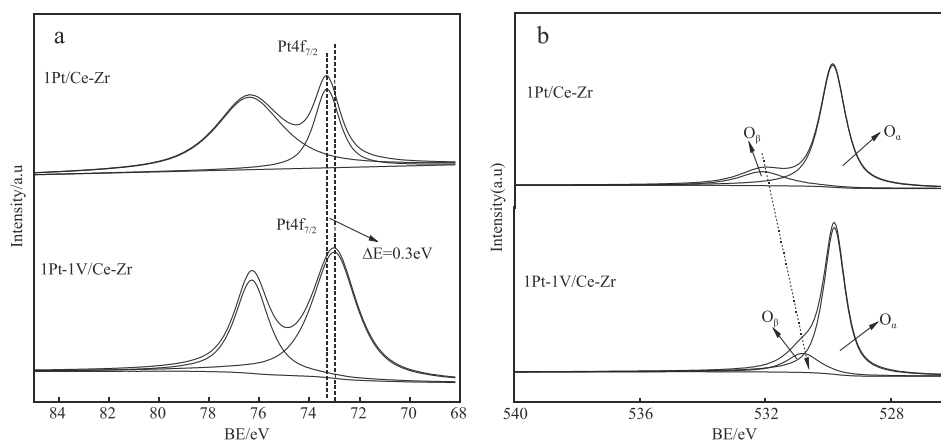


Fig. 9 – XPS (X-ray photoelectron spectroscopy) spectra for (a) Pt 4f, (b) O1s of 1Pt/Ce-Zr, 1Pt-1V/Ce-Zr catalysts.

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