Deactivation Mechanism of Arsenic and Resistance Effect of SO_4^{2-} on Commercial Catalysts for Selective Catalytic Reduction of NO_x with NH_3

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Abstract

Arsenic (As) is found to be poisonous to the commercial $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalysts for selective catalytic reduction of NO_x with NH_3 . The NO_x conversion of catalysts declines and N_2O formation dominates at high temperature (above 300 °C) after As poisoning. A series of activity and characterization experiments are applied to reveal the deactivation mechanism caused by As. Results indicate that doping of As on the catalysts, which exists as H_2AsO_4^- and HAsO_4^{2-} , doesn't seriously change surface area of catalysts or TiO_2 phase, but greatly decreases both the Lewis and Brønsted acid sites. It is found that V-OH is destroyed and less reactive As-OH is newly formed. V-OH site is crucial to the NH_3 adsorption and its destruction by As contributes to catalyst deactivation. Besides, stronger oxidizability of catalysts that resulted from more surface-active oxygen aroused by As leads to substantial non-selective catalytic reduction reaction and NH_3 oxidation at high temperature. Both of these two aspects result in lower NO_x conversion and higher N_2O formation. However, SO_4^{2-} can provide remarkable surface acidities and the sites that destroyed by As can thus be supplied. Benefited from these new reactive acid sites, catalysts with prominent SO_4^{2-} loading show superior arsenic resistance even with a high As content, which indicate to be a promising anti-poisoning formula. Finally, mechanism of arsenic poisoning and resistance effect of SO_4^{2-} is proposed based on the above analysis.

Key words: SCR catalysts; arsenic; deactivation; acidity; oxidizability

1 Introduction

Nitrogen oxides (NO_x) are one of the main pollutants in the atmosphere and greatly contribute to the formation of acid rain and particulate matter. NO is the majority (> 90%) of the NO_x and selective catalytic reduction (SCR) of NO with NH₃ has been widely used to abate NO from stationary sources: [1]

However, V₂O₅-WO₃/TiO₂ and V₂O₅-MoO₃/TiO₂, which are used as commercial catalysts, can be affected by poisonous elements in the flue gas such as alkali / alkaline-earth metals and heavy metals (arsenic and lead).[2-5] Extensive research has been done to reveal the deactivation mechanism by alkali metals: decrease in the surface acidity and redox reactivity.[6-9] Calcium and lead are also found to be poisonous to the SCR catalysts.[2, 3, 5, 10]

Arsenic does a significant damage to commercial catalysts as well. It presents as As₂O₃ or As₄O₆ in the gas phase and can be accreted on catalysts surface in the form of As₂O₅. [11, 12] Although several works have been published to elucidate the influence of arsenic and allege that arsenic can block up the micropore of catalysts and mainly destroy the surface acidity,[2, 11, 13] debates on how arsenic reacts with catalyst components exist and specific deactivation mechanism by arsenic is still unclear. As for the resistance of arsenic, Hums et al. reported that MoO₃ are found to be more competitive in tolerance to As compared with WO₃ in commercial SCR catalysts, [14, 15] but lower N₂-selectivity and NO_x conversion at high temperature of V₂O₅-MoO₃-TiO₂ [16] make it not as widely used as V₂O₅-WO₃-TiO₂. Up to now,

there has been no effective way to avoid As-poisoning of V₂O₅-WO₃-TiO₂ catalysts.

It is known that surface sulphates (SO₄²⁻) can be formed on SCR catalysts in the presence of SO₂ and can transform into strong Brønsted acid sites,[2, 17] thereby increasing the number of available sites for adsorption and activation of NH₃ and hence promoting the SCR reaction.[18, 19] In fact, commercial SCR catalysts always contain about 0.5-1% of sulfur, which mostly exists in the form of sulphate on the surface, due to the preparation method of TiO₂. [20] It is also feasible in the industry application to dope SO₄²⁻ during the impregnation procedure. Thus, SO₄²⁻ has a potential to be valid in the As resistance. However, few research [2] has been done to evaluate the effect of SO₄²⁻ on the As deactivation.

In this study, fresh and deactivated catalysts from a power plant in southwest China are systematically analyzed with SCR activity and characterization experiments. Our work tries to clarify the deactivation mechanism of arsenic on commercial catalysts. Besides, a feasible way that catalysts with high SO₄²⁻ content to resist the As deactivation is also explored in this work.

2 Experimental

2.1 Catalysts preparation

Both the fresh and deactivated catalyst samples are in the same series from a power plant in southwest China. To study the influence of arsenic on catalysts, the windward and the leeward side of the deactivated samples were distinguished. All these catalysts were crushed and sieved within 40-60 meshes for activity

measurement and signed as #0 for the fresh, #1 for the windward and #2 for the leeward.

2.2 Catalyst activity and NH₃ oxidation tests

SCR activity measurement was performed in a fixed-bed quartz reactor containing 200 mg of catalysts and operated under atmospheric pressure at 150-450 °C. The feed gas composed of 800 ppm of NO, 800 ppm of NH₃, 5 vol.% O₂, 500 ppm of SO₂ (when used), 5 vol.% H₂O (when used) and N₂ as the balance gas. Total flow rate was 500 mL/min, and the corresponding gas hourly space velocity (GHSV) was 150 000 mL/g·h. Concentrations of NO, NO₂, N₂O, and NH₃ were measured by an FT-IR spectrometer (Gaset DX 4000 FT-IR). The SCR activity of catalysts is expressed by the equation:

$$X_{NOx} = \frac{C_{in} - C_{out}}{C_{in}} \times 100\%$$

Where NO_x is the sum of NO, NO₂ and N₂O, C_{in} is the inlet concentration of NO_x, C_{out} is the outlet concentration of NO_x.

Experiments of the NH₃ oxidation were performed on the same reactor and operated under the same conditions except for no NO in the feed gas. NH₃ oxidation is calculated by:

$$X_{NH_3} = \frac{C_{in} - C_{out}}{C_{in}} \times 100\%$$

Where C_{in} is the inlet concentration of NH₃, C_{out} is the outlet concentration of NH₃.

2.3 Catalyst characterization

BET surface areas were measured by N₂ adsorption at 77K using an Autosorb-1-C (Quantachrome Instrument Crop.).

X-ray fluorescence (XRF) and ICP with an IRIS Intrepid II apparatus were collected to analyze chemical compositions of the catalysts.

X-ray diffraction (XRD) measurements were taken on a Rigaku D/max 2550PC system with Cu K α radiation, and crystalline phases were identified by comparison with the reference data from International Center for Diffraction Data (ICDD) files.

Raman spectra were obtained using a Raman spectrometer (LabRamHRUV, Jdbin-Yvon, France) with Raman shift from 50 to 2000 cm⁻¹ under the 514 nm excitation laser light at room temperature.

X-ray photoelectron spectroscopy (XPS) data were obtained with a Thermo ESCALAB 250 using Al K α X-ray (h ν =1486.6 eV) as a radiation source at 150 W. The binding energy was referenced to the C 1s line at 284.8 eV and peaks were deconvoluted after subtraction of the Shirley background using a sum of Lorentzian/Gaussian functions.[1]

Temperature-programmed reduction (TPR) of H₂ was carried out on a chemisorption analyzer (Micromeritics, AutoChem II 2920) under 10% H₂ in argon with a flow rate of 30 cm³/min. The temperature was increased from 50 °C to 900 °C at a rate of 10 °C/min.

Temperature-programmed desorption (TPD) of NH₃ was performed in the fixed-bed quartz reactor mentioned above. Prior to the NH₃-TPD test, each sample

(0.4 g) was preheated in N₂ (800 mL/min) gas at 350 °C for 2 h and then cooled down to 100 °C. After that, samples were exposed to a flow of 800 ppm NH₃ in N₂ (500 mL/min) for 1 h and then purged by a N₂ sweep (500 mL/min) for 1 h. Finally, the temperature was elevated from 100 °C to 500 °C at a rate of 5 °C/min and the desorbed NH₃ was continuously monitored by a Gasmet DX-4000 FT-IR detector.

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was recorded on a Nicolet 6700 spectrometer equipped with a Harrick IR cell and an MCT detector cooled by liquid N₂. Before the in-situ FT-IR tests, catalysts were heated to 350 °C under N₂ at a total flow rate of 100 mL/min for 2 h to remove adsorbed impurities. The background spectrum was collected in a flowing N₂ atmosphere and subtracted from the sample spectra. Samples were kept for 30 min at the desired temperature before scanning and the spectra were collected by accumulating 64 scans at a resolution of 4 cm⁻¹.

3 Results and Discussion

3.1 Chemical analysis and structure

Element content of the catalysts is shown in Table 1. To accurately measure the arsenic content, both the ICP and XRF results were collected. It is found that As content on the poisoned #1 is much higher than that on the fresh and poisoned #2, as with the SO₃ content which represents the loading of SO₄²⁻. This is due to the enrichment of arsenic and sulphates such as NH₄HSO₄ on the windward side. Other additives remnants do not change much after being exposed to the flue gas according

to XRF and XPS results (XPS profiles of K, Ca and Na are presented in Figure S1 in the Supporting Information), especially K_2O , CaO and Na_2O , which are thought to be severely poisonous to commercial SCR catalysts. Therefore, the catalysts can be defined as merely poisoned by arsenic.

Textural properties of catalysts are summarized in Table 2. Compared with the fresh, BET surface area and total pore volume of the poisoned #1 (windward) decrease obviously, while the average pore diameter improves to a certain extent, which can be attributed to the blocking of micropore by fly ash and sulphates. However, only slight changes, which are related to the inevitable thermal aging effect, appear on the poisoned #2 (leeward). It seems that the decrease of surface area or pore volume is not the main reason for arsenic poisoning of #2.

X-ray powder diffraction (XRD) patterns and Raman spectra were recorded to analyze the phase change of catalysts. As shown in Figure 1, only anatase TiO_2 presents on all these three samples from the XRD results. And all the catalysts produced Raman peaks at 145, 197, 395, 515, and 637 cm^{-1} in Figure 2, which correspond to the anatase phase of TiO_2 . [21-23] Both results indicate that arsenic at a certain amount (As_2O_3 3.37% on the poisoned #1 and As_2O_3 2.48% on the poisoned #2) does not bring changes to the crystalline phase of catalysts.

3.2 SCR activity and NH_3 oxidation

Figure 3 presents the SCR activity results of three samples. NO_x conversion of the poisoned catalysts declines and deteriorates above $350\text{ }^{\circ}C$, especially that of the

poisoned #2, which drops to around 40% at 450 °C compared to about 70% of the poisoned #1 and more than 95% of the fresh. It is interesting to find that the poisoned #1 has a much better SCR activity with a higher arsenic content (As_2O_3 of 3.37%), while NO_x conversion of the poisoned #2 decreases heavily with a lower content of 2.48%, which disagrees with common expectations. Actually, according to Chen's and Hums' results, catalysts with higher As content should have lower NO_x conversion. [2, 15] However, it should be aware that the poisoned #1 has a higher SO_4^{2-} content (represented as SO_3 of 3.54% in the XRF results compared to about 1% on the fresh and poisoned #2), which can promote SCR activity because of the enhancing surface acidities provided by SO_4^{2-} according to the previous research.[2, 17-19] Thus, higher SO_4^{2-} loading on the poisoned #1 could account for the better SCR activity.

In order to confirm the resistance effect of SO_4^{2-} and study the influence of SO_2 and H_2O , activity tests at 350 °C were performed in the presence of SO_2 and H_2O (see Figure S2 in the Supporting Information). Before adding H_2O or SO_2 , the SCR reaction had been stabilized for 1 h and almost the same NO_x conversion as those in Figure 3 are obtained. When 500 ppm SO_2 was added to the feed stream, NO_x conversion slowly increased. During the 4 h, NO_x conversion of three samples increased from 91% (fresh), 84% (poisoned #1) and 53% (poisoned #2) to around 93%, 87% and 57%, respectively. After that, 5 vol.% H_2O was also added and it is found that NO_x conversions were almost steady. The activity improvements in this experiment should be attributed to the enhanced surface acidities from SO_2 sulfuration,

as emphasized above. Therefore, these tests verified that SO_4^{2-} can improve the NOx conversions of three samples, especially that of the poisoned. Combining results here and above, it is convinced that SO_4^{2-} could act as an effective As-resistance additive.

Based on the N_2O concentration results in Figure 3, it is observed that N_2O formation is almost the same below 300 °C among three samples and begins to differentiate at a higher temperature, which coincides with the tendency of activities. These results are generally in line with Peng's work, even though his N_2O formation is lower than ours, [13] which could be due to the different catalyst samples and reaction conditions. In Figure 3, N_2O formation of two poisoned samples grows dramatically above 350 °C and the poisoned #2 yields the largest, which is probably related to its intensive decrease in the NOx conversion at high temperature. Actually, N_2O is the by-product of the NH_3 -SCR reaction, i.e., non-selective catalytic reduction (NSCR): [16, 24, 25]

N_2O also comes from NH_3 oxidation: [24, 26]

which means that the poisoned samples have a much lower N_2 -selectivity and may arouse strong NSCR and NH_3 oxidation at high temperature.

To verify the hypothesis above, this work performed NH_3 oxidation experiments of three catalysts. The NH_3 oxidation and N_2O formation results are presented in Figure 4 (a) and 4 (b), respectively. Much stronger NH_3 oxidation occurs on two poisoned samples and about 30% of NH_3 is oxidized at 450 °C. It seems that more

NH₃ participating in NH₃ oxidation while less in SCR reaction contribute to the poor activity performance of two poisoned samples at high temperature. Figure 4 (b) shows the N₂O formation and it is obvious that N₂O forms significantly on two poisoned samples above 350 °C. However, N₂O formation at 450 °C here (27 ppm of #1 and 20 ppm of #2) is far less than that in activity tests (107 ppm of #1 and 154 ppm pf #2), indicating the notable occurrence of NSCR reaction on two poisoned samples and especially on the poisoned #2. Thus the huge reduction of NO to N₂O instead of N₂ leads to the low NO_x conversion as well. Besides, considerable NH₃ oxidation also occurs on the fresh at high temperature while excellent activity results and rather small N₂O formation are still obtained. This is due to the good N₂-selectivity of fresh V₂O₅-WO₃/TiO₂ catalysts in SCR and selective catalytic oxidation and the fact that most of the NH₃ participates in the SCR reaction with NO instead of NH₃ oxidation at high temperature.[24, 27-30]

3.3 XPS analysis

XPS analysis is used to figure out the way arsenic influences catalyst components. As 3d patterns of poisoned #1 and poisoned #2 are shown in Figure 5 (a) and fitted into 2 peaks. Only As⁵⁺ is observed on both samples and as published by Wagner [31], Soma [32], and Zhang [33], peaks at 45.7 eV and 46.6 eV can be referred to as HAsO₄²⁻ and H₂AsO₄⁻, respectively. It accords with Peng's and Hilbrig's results that the majority oxidation state of arsenic species on commercial SCR catalysts surface is As⁵⁺ and the species can be associated with an orthoarsenate (V).[13, 34]

Figure 5 (b) shows O 1s spectra of three samples. The O 1s line are fitted into four

peaks and ratio of integral area of these peaks are listed in Table 3. According to the handbook of XPS [31] and studies of several investigators,[5, 35-37] peaks at 530.1-530.6 eV are assigned to the lattice oxygen in metal oxides, those from 531.1 eV to 532.1 eV are related to the ionization of oxygen species that allows compensations for some deficiencies in the subsurface of transition metals, and peaks at around 533 eV are caused by hydroxyl species and/or adsorbed water species. Thus, peaks at 531.3 and 531.1 eV can be referred to the oxygen in M=O and M-O-M, and peaks at 532.1 eV are assigned to M-O (M represents metals on the catalysts surface).[35, 36] Besides, oxygen in M=O, M-O-M and M-O belongs to the surface-active oxygen, [36-38] which is more active in oxidation than the lattice oxygen. From Table 3, it is obvious that the poisoned catalysts have a much higher ratio (28.44% for #1 and 34.55% for #2) of the surface-active oxygen than the fresh one (18.37%), which is due to the transformation from lattice oxygen under the effect of arsenic, and could account for the much stronger oxidizability of the poisoned #1 and #2.

3.4 Redox properties and surface acidities

Figure 6 presents H₂-TPR profiles of three samples in the range of 100-900 °C. Two reduction peaks are observed on the fresh and poisoned #2. The peak at 460 °C on the fresh is corresponding to the coreduction of V⁵⁺ to V³⁺ and W⁶⁺ to W⁴⁺ that is in the vicinity of surface vanadium oxide species; while peaks at 783 and 760 °C can be attributed to the reduction of W⁴⁺ to W⁰. [39, 40] Peaks at 401 °C and 440 °C with a shoulder at 421 °C on the poisoned samples belong to the overlap of V⁵⁺ to V³⁺, W⁶⁺

to W^{4+} , and As^{5+} to As^0 . [13, 40] It is clear that the main reduction peaks of poisoned samples are larger than the fresh, which means a larger H_2 consumption due to the reduction of As^{5+} . Furthermore, the main reduction peaks of poisoned samples shift towards lower temperature and the poisoned #2 shows the largest extent, indicating that catalysts oxidizability becomes stronger under the effect of arsenic and the poisoned #2 has the strongest oxidizability. These results are ascribed to the higher ratio of surface-active oxygen on the poisoned #1 and #2, as mentioned above.

Figure 7 (a) shows the NH_3 -TPD profiles of three samples. All curves exhibit multiple peaks. To better explain the NH_3 desorption profiles, deconvolutions are performed and the results are shown in Figure 7 (b)-(d). Three peaks can be observed on the fresh and poisoned #1, while only two present on the poisoned #2. Peaks 1 at 170-183 °C, peaks 2 at 252-274 °C and peaks 3 at 341-378 °C are assigned to the desorption of physisorbed, weakly chemisorbed, and strongly chemisorbed of NH_3 , respectively. [13, 41] Integral area of these peaks represents surface acidities and the results are listed in Table 4. To eliminate the influence of surface area, integral results are divided by BET surface area (S_{BET}) from Table 2 and the ratio data, which are used to analyze surface acidities, are also shown in Table 4. Compared to the fresh, the total acidity of the poisoned #2 declines apparently (about 18%), including partial weak acidities of peak 2 and all of strong acidities of peak 3. It is inferred that destruction of partial weak acid sites and most of the strong acid sites by As contributes to the deactivation. However, the acidity of the poisoned #1 enhances dramatically, which should benefit from the high SO_4^{2-} loading. As is widely accepted

that NH_3 adsorption is important for SCR, [27, 42, 43] the stronger acidity of the poisoned #1 can support its good performance in the SCR activity tests. Besides, NH_3 desorption of the two poisoned samples ends at around 400 °C while the fresh one continues to 500 °C, which is another evidence of the strong acid sites destroyed by arsenic.

3.5 FT-IR analysis

The FT-IR spectra of three samples are shown in Figure 8. Two spectral regions (3800-3000 cm^{-1} for the OH region and 2000-900 cm^{-1} for the fingerprint region) are presented separately for a better display. Bands at 3695 cm^{-1} and 3634 cm^{-1} observed on the fresh are due to the surface hydroxyl groups bonded to titanium (Ti-OH) [11, 44] and vanadium (V-OH) [27-29, 45], respectively. According to Ramis et al.[46], Ti-OH and W-OH stretching bands are expected in the same frequency region, therefore, bands at 3695 cm^{-1} may also contain W-OH. From Figure 8 (a) it can be found V-OH vanished and Ti-OH weakened after poisoned by arsenic, which belong to the destruction of strong and weak acid sites respectively. These results coincide well with the NH_3 -TPD analysis. Based on the SCR reaction mechanism proposed by Topsøe [27-29, 47], the V-OH Brønsted acid site is crucial and responsible for the adsorption of NH_3 . Therefore, it can be supposed that the destruction of V-OH by arsenic contributes to the catalyst deactivation. Besides, bands at 3450 cm^{-1} and in the range of 3400-3100 cm^{-1} are attributed to the adsorbed water species and N-H stretching mode of the adsorbed NH_3 species, respectively.[28, 29] The increasing of these bands on the two poisoned samples is owing to their exposing to flue gas in the

power plant.

Results of the fingerprint region at low wavenumber are shown in Figure 8 (b). Bands at 1635 cm^{-1} and 1132 cm^{-1} are assigned to the adsorbed water species [28, 29] and S=O symmetric stretching of sulphates [17, 48] respectively, and the poisoned #1 shows a much stronger band of the latter one, which indicates an abundance of SO_4^{2-} and accords with the XRF results. The bands at 1040 cm^{-1} that belong to the surface vanadyl species [46] are present on the fresh and poisoned #2, inferring that V=O Lewis acid sites are not seriously affected by arsenic at a certain content (#2: As_2O_3 of 2.48%). However, this band dismisses at a higher arsenic content (#1: As_2O_3 of 3.37%) and a new weak broad band appears at 1068 cm^{-1} on the poisoned #1, whose assignment is not clear according to the relevant research. Considering As electronic withdrawing and high content of SO_4^{2-} and As on the poisoned #1, partial transformation from S=O to S-O-As seems a reasonable explanation. Actually, previous research has been reported that peaks at 1060 cm^{-1} [49] and 1078 cm^{-1} [37] are ascribed to bands of S-O complexes. Thus, the weak broad band at 1068 cm^{-1} tentatively assigned to a S-O-As structure could be reasonable.

3.6 In situ FT-IR spectra of NH_3 -TPD analysis

Figure 9 shows the in situ FT-IR spectra obtained upon adsorption of NH_3 at $100\text{ }^\circ\text{C}$ over three samples and then evacuation at increasing temperature. In the spectrum recorded at $100\text{ }^\circ\text{C}$, the negative spikes at 3650 cm^{-1} on the fresh are attributed to the NH_3 adsorption on V-OH [27-29] while those on the poisoned at 3616 cm^{-1} and 3613 cm^{-1} are related to NH_3 adsorption on As-OH.[11] These results agree

with the conclusion from Figure 8 (a) that V-OH is destroyed by arsenic and can also verify the formation of As-OH. Bands in $3400\text{--}3100\text{ cm}^{-1}$, $1300\text{--}1150\text{ cm}^{-1}$ and peaks at around 1600 cm^{-1} are assigned to NH_3 adsorption on the Lewis acid sites, whereas bands at around 3050 cm^{-1} , 1670 cm^{-1} and 1430 cm^{-1} belong to the NH_4^+ on Brønsted acid sites.[13, 27-29] As shown in Figure 9, it is obvious that both Lewis and Brønsted adsorption on the poisoned #2 are much weaker and dismiss rapidly as temperature elevating, indicating its decreasing and unstable surface acidities. Moreover, two new bands at 1542 cm^{-1} and 1452 cm^{-1} that are assigned to the NH_2 -amide [24, 26] group and NH imido species [24, 50] respectively appear on the spectra of two poisoned samples. According to the published results,[24, 26, 51] NH_2^- , coming from the coordinated NH_3 on Lewis acid sites, is thought to be intermediate species of NH_3 oxidation and can be further oxidized to NH which reacts with gaseous NO to form N_2O (i.e., NSCR). Thus, the appearance of NH_2^- amide group and NH imido species can serve as a convictive evidence for the existence of NH_3 oxidation and NSCR on the poisoned samples at high temperature. NH_3 oxidation at high temperature is also confirmed in Peng's work, [13] but here the existence of NSCR on the As poisoned catalysts is verified as well and it is concluded that NSCR contributes primarily to the huge N_2O formation on two poisoned samples at high temperature, as described above.

As for the poisoned #1, it is unusual to find that NH_3 adsorption on Brønsted and Lewis acid sites decreases unobviously even though its As content is higher and vanadium acid sites (V-OH and V=O) are destroyed. The high SO_4^{2-} content could

account for this phenomenon. It has been reported that both Lewis and Brønsted acid sites are generated when a sulfate ion is introduced into TiO₂. [17, 44, 52] Therefore, NH₃ can adsorb on these newly formed acid sites, which agrees with NH₃-TPD results, and the surface acidities that destroyed by As can thus be supplied.

3.7 Mechanism of arsenic poisoning and resistance effect of SO₄²⁻

To study mechanism of As poisoning and resistance effect of SO₄²⁻, in situ FT-IR over three catalysts was carried out at 350 °C. Results are shown in Figure 10. Firstly, the samples that pretreated in N₂ were purged by 1000 ppm NH₃ for 1 h at 350 °C and then induced by N₂ for 30 min to remove physical adsorbed NH₃. Negative spikes at around 3650 cm⁻¹ and 3610 cm⁻¹ can be found after NH₃ adsorption, which are the same as Figure 9 and can be attributed to NH₃ adsorption on V-OH and As-OH respectively. The bands at 1370 cm⁻¹ are assigned to asymmetric stretching vibration modes of O=S=O [37] and negative spikes at this band demonstrate NH₃ adsorption on SO₄²⁻. Peaks at around 1540 cm⁻¹ and 1630 cm⁻¹ belong to NH₂⁻ and H₂O respectively while those at 1473 and 1332 cm⁻¹ can be attributed to nitrites [53]. On the fresh and poisoned #2, only Lewis acid sites (3352, 3259, 1253, 1224 cm⁻¹ on #0 and 3347, 3263 cm⁻¹ on #2) [27-29] but no Brønsted sites observed, which is due to the better stability of Lewis NH₃ adsorption. [29] Just as the results from Figure 9, NH₃ adsorption on the poisoned #2 is extremely slight, reflecting its poor acidity at high temperature. After NO and O₂ pass over three samples, adsorbed NH₃ species weakens and disappears within 5 min, while some new peaks occurs, locating at 3634, 1653, 1620, 1377, 1374, 1528 and 1210 cm⁻¹. These peaks can be assigned to new OH

groups bonded to more oxidized V species (3634 cm^{-1} on #0), bridging nitrate (1653 cm^{-1} on #0), H_2O (1620 cm^{-1} on #0), NH_4NO_3 (1377 cm^{-1} on #0 and 1374 cm^{-1} on #1), NH_2^- amide group (1528 cm^{-1} on #2) and bridging nitrite (1210 cm^{-1} on #1).[29, 51, 53] Nitrites and nitrates, especially NH_4NO_3 , are thought to be intermediates during SCR reaction,[24, 53] and formation of such species verifies the occurrence of SCR reaction on the fresh and poisoned #1 at $350\text{ }^\circ\text{C}$. However, no nitrate or nitrite but some NH_2^- amide group is observed on the poisoned #2, indicating that its NSCR and NH_3 oxidation compete with SCR reaction at high temperature. All these results agree well with the NO_x conversion at $350\text{ }^\circ\text{C}$ in the activity tests. It should also be noticed that after introducing NO and O_2 , smaller negative spikes of NH_3 adsorption on As-OH weaken but still exist on the poisoned #2, while larger ones of $\text{O}=\text{S}=\text{O}$ vanish completely on the fresh and poisoned #1, inferring that NH_3 adsorption on SO_4^{2-} is reactive while As-OH is less.

Special attention should be paid to spectra of the poisoned #1. As is shown in Figure 10 (b), much stronger Lewis NH_3 adsorption (3258 and 1272 cm^{-1}) and obvious Brønsted NH_3 adsorption (1430 cm^{-1}) are obtained, which confirms that the high content of SO_4^{2-} can provide both Lewis and Brønsted acid sites. Besides, peaks of these adsorbed NH_3 species and NH_2^- amide group dismiss when NO and O_2 are introduced 5 min and become negative after that. It may be due to the existence of some NH_3 and NH_4^+ on the poisoned #1 even after N_2 pretreating at $350\text{ }^\circ\text{C}$ and they begin to react with NO and O_2 when the adsorbed NH_3 species is consumed. These results confirm the remarkable acidity and reactivity of SO_4^{2-} and interpret its superior

resistance effect.

According to the analysis above, the proposed deactivation mechanism of arsenic is shown in Scheme 1 (ads: adsorption, oxy: oxidized. The same in Scheme 2). NH_3 cannot adsorb on V-OH anymore on account of its destruction by arsenic, which contributes to the decrease of surface acidities. In contrast, the oxidizability is enhanced because of more surface-active oxygen raised by arsenic and NH_3 that coordinates on V=O Lewis acid sites can be oxidized into N_2O and/or NO (not shown in Scheme 1 or Scheme 2) through the amide group (NH_2^-) at high temperature (above $300\text{ }^\circ\text{C}$). Besides, the formed NH_2^- can be further oxidized into NH and then reacts with gaseous NO to produce N_2O (i.e. NSCR). Thus, severely weakened surface acidities and less NH_3 participating in the SCR reaction but more in the competitive NSCR and NH_3 oxidation at high temperature lead to the catalysts deactivation by arsenic.

Based on these experiment results and deactivation mechanism, it is convincing that SO_4^{2-} provides remarkable reactive surface acidities, which could supply Lewis and Brønsted acid sites that destroyed by arsenic. NH_3 can adsorb on these newly formed acid sites and then completes the SCR reaction normally, as shown in Scheme 2. Therefore, SO_4^{2-} indicates to be an effective supplement for commercial catalysts for resistance of arsenic.

4 Conclusions

Arsenic causes serious deactivation of commercial $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalysts for the selective catalytic reduction of NO_x with NH_3 . A series of activity and

characterization experiments were carried out on the fresh and poisoned (the windward and the leeward side) catalysts from a power plant in southwest China. The results indicate that doping of arsenic on the catalysts, which exists as H_2AsO_4^- and HAsO_4^{2-} , doesn't seriously change textural properties such as surface area and TiO_2 phase, but greatly decreases both the Lewis and Brønsted acid sites. It is also found that V-OH is destroyed and less reactive As-OH is newly formed, which contributes to catalyst deactivation because NH_4^+ adsorbed on V-OH sites is crucial to the SCR reaction. On the other hand, catalyst oxidizability is enhanced because of the more surface-active oxygen aroused by arsenic, which leads to strong NSCR and NH_3 oxidation at high temperature (above 300 °C). Both of these two aspects result in the catalysts deactivation by arsenic. Remarkable surface acidities provided by SO_4^{2-} can supply those destroyed by As and benefited from these reactive acid sites, catalysts with prominent SO_4^{2-} loading show superior arsenic resistance even with a high As content, which indicate to be a promising anti-poisoning formula.

Based on the above analysis, mechanism of arsenic poisoning and resistance effect of SO_4^{2-} are proposed: NH_3 can't adsorb on V-OH because of As destruction and at high temperatures (above 300 °C), NH_3 is oxidized to N_2O and/or NO (NH_3 oxidation) through NH_2^- , which can be further oxidized into NH and react with NO to produce N_2O (NSCR). Nevertheless, when there is SO_4^{2-} , NH_3 can adsorb on the newly reactive acid sites that provided by SO_4^{2-} and then complete the SCR reaction normally. Therefore, SO_4^{2-} could be an effective supplement for commercial $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalysts for resistance of arsenic.

Acknowledgements

The authors gratefully acknowledge the financial support of the National Science Foundation for Distinguished Young Scholars of China (No.51125025), the National High-Tech Research and Development (863) Program of China (No. 2013AA065401), and the Key Innovation Team for Science and Technology of Zhejiang Province (No. 2011R50017). The authors appreciate support from CPI YUANDA Environmental-Protection Engineering Co., Ltd.

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Table 1

Element content of the catalysts

Samples	Elements content (wt.%)							
	V ₂ O ₅	WO ₃	As ₂ O ₃	As ₂ O ₃ [*]	SO ₃	K ₂ O	Na ₂ O	CaO
Fresh	0.432	2.41	0	0	1.18	0.195	0.162	1.79
Poison #1	0.531	2.54	3.37	3.40	3.54	0.117	0.145	2.05
Poison #2	0.491	2.70	2.48	2.31	0.887	0.103	0.167	2.06

^{*} Acquired from ICP results. Others acquired from XRF results

Table 2

Textural properties of the catalysts

Samples	BET surface area (m ² /g)	Total pore volume (cm ³ /g)	Average pore diameter (nm)
Fresh	58.35	0.2471	15.188
Poison #1	39.32	0.1804	16.366
Poison #2	50.7	0.2259	15.643

Table 3

Ratio of integral area of O 1s peaks in Figure 5 (a)

Samples	Lattice oxygen	M=O & M-O-M	M-O	ads H ₂ O	Surface-active oxygen [*]
Fresh	78.36%	10.09%	8.28%	3.27%	18.37%
Poison #1	63.74%	21.00%	7.44%	7.82%	28.44%
Poison #2	62.88%	25.97%	8.58%	2.57%	34.55%

^{*}Sum of M=O & M-O-M and M-O.

Table 4

Surface acidities of the catalysts.

Samples	Total ^a	Peak 1 ^b	Peak 2 ^b	Peak 3 ^b	Total / S _{BET} ^c	Peak 1 / S _{BET} ^c	Peak 2 / S _{BET} ^c	Peak 3 / S _{BET} ^c
Fresh	15460	4532	10702	5110	265	77.7	183.4	87.6
Poison #1	32912	8289	21353	7331	837	210.8	543.1	186.4
Poison #2	11027	4377	8483	0	217	86.3	167.3	0

^a Integrated from NH₃-TPD profiles of three samples;^b Integrated from the deconvolution results of three samples;^c S_{BET} acquired from BET results in Table 2.

Figure captions

Figure 1. XRD patterns of the three samples.

Figure 2. Raman spectra of the three samples.

Figure 3. Comparisons on the SCR performance of fresh and two poisoned catalysts.

Reaction conditions: catalyst mass = 200 mg, $[\text{NO}] = [\text{NH}_3] = 800$ ppm, $[\text{O}_2] = 5$ vol%, total flow rate = 500 mL/min, GHSV = 150 000 mL/g·h.

Figure 4. NH_3 oxidation of fresh and two poisoned catalysts. Reaction conditions: catalyst mass = 200 mg, $[\text{NH}_3] = 800$ ppm, $[\text{O}_2] = 5$ vol%, total flow rate = 500 mL/min, GHSV = 150 000 mL/g·h. (a) The N_2O and (b) NO_x formation of the three samples.

Figure 5. XPS spectra of (a) As 3d and (b) O 1s of the three samples.

Figure 6. H_2 -TPR profiles of the three samples.

Figure 7. (a) NH_3 -TPD profiles of the three samples and the deconvolution results of (b) fresh, (c) poisoned #1 and (d) poisoned #2.

Figure 8. FTIR spectra of the three samples at (a) high wavenumber and (b) low wavenumber.

Figure 9. In situ FT-IR spectra of NH_3 -TPD of (a) fresh, (b) poisoned #1 and (c) poisoned #2 catalysts.

Figure 10. In situ FT-IR spectra of (a) fresh, (b) poisoned #1 and (c) poisoned #2 catalysts pretreated by 1000 ppm NH_3 , and then followed by exposing to 1000 ppm NO and 5% O_2 at 350 °C.

Scheme 1. Arsenic poisoning mechanism.

Scheme 2. Resistance effect of SO_4^{2-} .

Figure 1. XRD patterns of the three samples.

Figure 2. Raman spectra of the three samples.

Figure 3. Comparisons on the SCR performance of fresh and two poisoned catalysts. Reaction conditions: catalyst mass = 200 mg, [NO] = [NH₃] = 800 ppm, [O₂] = 5 vol%, total flow rate = 500 mL/min, GHSV = 150 000 mL/g·h.

Figure 4. NH₃ oxidation of fresh and two poisoned catalysts. Reaction conditions: catalyst mass = 200 mg, [NH₃] = 800 ppm, [O₂] = 5 vol%, total flow rate = 500 mL/min, GHSV = 150 000 mL/g·h. (a) The NH₃ oxidation and (b) N₂O formation of three samples.

Figure 5. XPS spectra of (a) As 3d of two poisoned samples and (b) O 1s of the three samples

Figure 6. H₂-TPR profiles of the three samples.

Figure 7. (a) NH_3 -TPD profiles of the three samples and the deconvolution results of (b) fresh, (c) poisoned #1 and (d) poisoned #2.

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Scheme 1 Arsenic poisoning mechanism

Scheme 2 Resistance effect of SO_4^{2-}