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Using vanadyl sulfate to prepare carbon-supported vanadium catalyst for flue gas desulfurization

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Abstract：Vanadyl sulfate（$V^{IV}OSO_4$）was used to prepare carbon-supported vanadium catalyst for flue gas desulfurization. The $V^{IV}OSO_4$ impregnated on activated carbon（AC）was easily oxidized into vanadium（V）sulfate phase（possibly $V_2O_3(SO_4)_2$）in air，which exhibited high catalytic activity toward SO_2 oxidation，thus significantly enhancing SO_2 retention on AC. Furthermore，the vanadium（V）sulfate can be decomposed upon calcination in nitrogen with optimum temperature of 500 ℃ to form vanadium（V）oxide，further improving SO_2 retention mainly due to increase in micorpore volume suitable for sulfate storage and showing suitability of vanadyl sulfate to prepare traditional V_2O_5/AC catalyst. To obtain fully oxidized vanadium oxides，preoxidation was carried out on catalyst after calcination. However，due to ablation of carbon support，reduction of vanadium and/or formation of surface oxygen groups，the preoxidation was negative for SO_2 retention. Additionally，this paper provided preliminary evidence indicating transformation of vanadium（V）oxide in V_2O_5/AC into vanadium（V）sulfate during desulfurization. Combined with catalytic role of vanadium（V）sulfate for SO_2 oxidation，SO_2 removal on V_2O_5/AC likely followed a mechanism that the vanadium（V）oxide firstly transformed into vanadium（V）sulfate and the latter was then responsible for subsequent SO_2 oxidation into H_2SO_4.

Keywords：V_2O_5/AC；SO_2 removal；vanadium（V）sulfate；catalytic role；low temperature

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Sulfur dioxide（SO_2）removal from combustion plants is a topic of ongoing research since it is one of the major precursors of acid rain[1~3]. The current techniques used in industry for SO_2 removal are mainly based on solid-gas reactions using dolomites or calcite as sorbents or in liquid-gas reactions with the active phases in aqueous solution[4,5]. However，all these processes generate considerable amounts of by-products requiring large space and high capital costs for their handling. Active coke/carbon based dry flue gas desulfurization technologies are expected to be increasingly preferred because SO_x，NO_x，Hg and VOC_s can be removed simultaneously and the SO_2 removed can be converted into valuable products under mild conditions[6~9]. Many AC supported catalyst/sorbents，such as CuO/AC[7]，V_2O_5/AC[9]，CaO/AC[10]，Fe_2O_3/AC[11] and MgO/AC[12]，have been developed for SO_2 removal. In particular，V_2O_5/AC has been found to be promising for industrial application due to its high SO_2 uptake at stack temperatures（120~200 ℃）and its mechanical strength for moving bed operation[9,13~15].

It has been reported that SO_2 removal on V_2O_5/AC is achieved via a mechanism including the following steps[13,14]：SO_2 adsorption，interaction of SO_2 with V_2O_5 to form $VOSO_4$-like intermediate，reaction of O_2 with $VOSO_4$-like intermediate to yield V_2O_5 and SO_3，and migration of SO_3 or H_2SO_4 formed through reaction between SO_3 and H_2O to adjacent AC pores. The crucial part of this mechanism is the intermediate role of $VOSO_4$-like species. Furthermore，Ma et al[13] proposed that pure $VOSO_4$ preloaded on AC can be readily converted into V_2O_5 and H_2SO_4 under actual SO_2 removal conditions. If it is true，V_2O_5/AC catalyst may be obtained via a very simplified way using $VOSO_4$ as precursor.

The main purpose of this work is to evaluate the suitability of vanadyl sulfate（$V^{IV}OSO_4$）for preparation of V_2O_5/AC catalyst for flue gas desulfurization. Effect of preparation conditions on SO_2 retention is studied using various characterization techniques. The mechanism of SO_2 removal over V_2O_5/AC catalyst is also discussed.

1 Experimental
1.1 Catalyst preparation

An activated carbon（AC，30~60 mesh）from

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Xinhua Chemical Plant with BET surface area of 910 m^2/g was used as support. Vanadyl sulfate ($V^{IV}OSO_4$) was impregnated by pore volume impregnation of AC with vanadium(IV) oxide sulfate trihydrate ($V^{IV}OSO_4 \cdot 3H_2O$) aqueous solution (1 mL solution/g AC). After impregnation, the catalysts with different preparation conditions were as follows: Cat50 was obtained by drying the impregnated sample in air at 50 ℃ for 12 h. Cat120 was obtained by drying Cat50 in air at 120 ℃ for 8 h. CatT was prepared by calcination of Cat120 in N_2 at desired temperature for 1 h. Cat250A and B were prepared by preoxidation of CatT in air at 250 ℃ for 3 h or 5 h, respectively.

The numeral in the name of catalyst represents the final treated temperature. The vanadium content of the resulting catalyst was determined by the concentration of $VOSO_4$ used and further confirmed by ICP analysis. Note that the $VOSO_4$ impregnated on AC was decomposed during calcinaion, and consequently there was 3.53% $VOSO_4$ initially impregnated in Cat50 and Cat120, and 2% V_2O_5 in the other catalysts.

1.2 Desulfurization measurement

A typical desulfurization measurement was conducted in a fix-bed quartz reactor (i. d. 22 mm) loaded with 3 g catalyst at 120 ℃. Simulated flue gas consisted of 0.15% SO_2, 4.5% O_2, 2.5 % H_2O and N_2 to balance. H_2O was introduced into the reactor by passing the N_2 through a heated gas-wash bottle containing deionized water. The total flue rate was maintained at 400 mL/min with GHSV of ~ 4 000 h^{-1}. The concentrations of SO_2 and O_2 in the outlet of the reactor were measured simultaneously by an on-line flue gas analyzer (KM 9106 Quitox, Kane-May International Limited).

1.3 Temperature-programmed experiment

Thermogravimetric Analysis (TG) was carried out in 50 mL/min N_2 on a thermogravimetric analyzer (NETZSCH, STA409PC) with a constant heating rate of 5 ℃/min. Temperature-programmed decomposition/desorption (TPDC/TPD) experiments were carried out in the desulfurization apparatus. 0.5 g sulfated catalyst was loaded in the reactor and then heated from room temperature to 500 or 900 ℃ in 400 mL/min N_2 at a constant heating rate of 5 ℃/min. The evolution of SO_2 was monitored simultaneously using the KM 9106 Quitox flue gas analyzer.

1.4 X-ray photoelectron spectroscopy (XPS)

A Thermo ESCALAB 250 spectrometer was used for the surface chemical composition study. An Al $K\alpha$ monochromatized radiation (1 486.6 eV) was employed as X-ray source. The high resolution spectra of the V $2p$ and O $1s$ were recorded with pass energy of 20 eV. The binding energy (BE) scales were corrected for charging effects by assigning a value of BE = 284.6 eV to the C $1s$ peak from the surface contamination. In order to separate elemental species in different oxidation states, the XPS was analyzed by curve-fitting routine with a Gaussian/Lorentzian product function after a Shirley background subtraction.

1.5 Surface area and pore structure analysis

The textural properties of the catalysts were measured through nitrogen adsorption at 77 K using ASAP 2020 Micromeritics analyzer. Prior to the measurements, Cat50 was degassed at 50 ℃ and the other catalysts at 120 ℃ for 5 h. Specific surface area was calculated from the N_2 adsorption isotherms by applying the Brunauer-Emmett-Teller (BET) equation. The micropore volume was obtained from the Dubinin-Radushkevich (DR) methods.

1.6 Elemental analysis

Carbon, hydrogen, oxygen, nitrogen and sulfur analyses of the catalysts were performed on a varioEL cube from Elementar Analysensysteme GmbH Germany.

2 Results

2.1 Determination of calcination temperature

To determine the calcination temperature, decomposition behaviors of pure $VOSO_4$ and that impregnated on AC were investigated. The results of temperature-programmed experiment are illustrated in Figure 1. As seen, Figure 1(a) shows three obvious stages for decomposition of $VOSO_4 \cdot 3H_2O$: A → B, B → C and D → E. The corresponding substance at the end of every stage could be determined by weight ratio. Results given in Table 1 show that the corresponding substances at B, C and E are $VOSO_4 \cdot H_2O$, $VOSO_4$ and V_2O_5, respectively. Attention is paid to the decomposition of $VOSO_4$, which starts at about 520 ℃ and ends at 600 ℃, indicating that the catalyst should be calcined at 600 ℃ or higher temperatures to obtain V_2O_5. However, Figure 1(b) gives a very different result. The release of SO_2 used to express decomposition of $VOSO_4$ impregnated on AC is detected between 260 and 530 ℃ with a maximum at 375 ℃, indicating the promoting effect of AC for $VOSO_4$ decomposition. Similar phenomenon is also observed for NH_4HSO_4. When it is impregnated on AC, the decomposition of NH_4HSO_4 becomes much easier than that of pure substance because carbon could act as reducing agent to reduce it into SO_2[16].
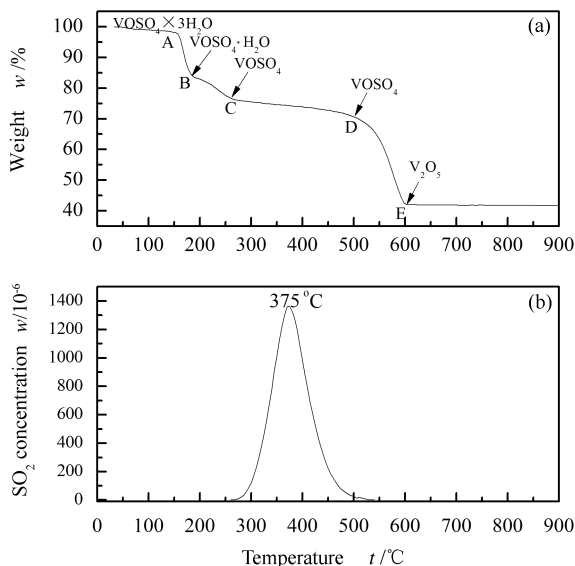
Cat500 will be emphasized.

Figure 1   TG of $VOSO_4 \cdot 3H_2O$ (a)
and SO_2 release profile of Cat120 during TPDC (b)
experimental conditions：50 mL/min N_2 for TG，
400 mL/min N_2 for TPDC, heating
rate of 5 ℃/min for both cases

Table 1   Theoretical and actual weight ratios of corresponding substances at B，C and E

	$VOSO_4 \cdot H_2O$	$VOSO_4$	V_2O_5
Theoretical weight ratio $w/\%$	83.4	75.1	41.9
Actual weight ratio $w/\%$	83.9[B]	75.4[C]	42.3[E]

2.2   Desulfurization measurement

    The desulfurization results are illustrated in Figure 2. In all runs, the measurements are terminated when SO_2 conversion decreases from 100% to 90%, as shown in Figure 2(a). The SO_2 retention is quantified by integrating curve area and expresses as $mg_{SO_2}/g_{catalyst}$. Clearly, SO_2 retention is not the value at saturation and depends on not only SO_2 concentration in the feed but also space velocity of flue gas. As seen from Figure 2(b), SO_2 retention on AC is greatly enhanced by loading vanadium to a value comparable to that of Ca-based sorbent[10], which is related to catalytic activity of vanadium toward SO_2 oxidation. Particularly, it is interesting to see that Cat50 and Cat120, the catalysts only dried at low temperatures without any additional treatment, exhibit high SO_2 removal efficiency. According to the proposal by Ma et al[13], the $VOSO_4$ impregnated on AC was readily converted into H_2SO_4 and V_2O_5 during desulfurization, leading to activation of catalysts and hence the enhancement of SO_2 retention. However, XPS and TPD results presented later show that this is not the real reason.

    It is suggested that the promoted decomposition of $VOSO_4$ on AC is probably a result of carbon reduction. Hence, present work will investigate calcination temperature in the range of 400 ~ 550 ℃. Catalysts calcined at 400, 450, 500 and 550 ℃ are applied to desulfurization. The results show that under given conditions Cat500 and Cat550 exhibit same SO_2 retention of 56.9 mg/g, which are higher than those of Cat400 and Cat450 (45.6 mg/g), suggesting that $VOSO_4$ impregnated on AC could be completely decomposed upon calcination at 500 ℃. Therefore,
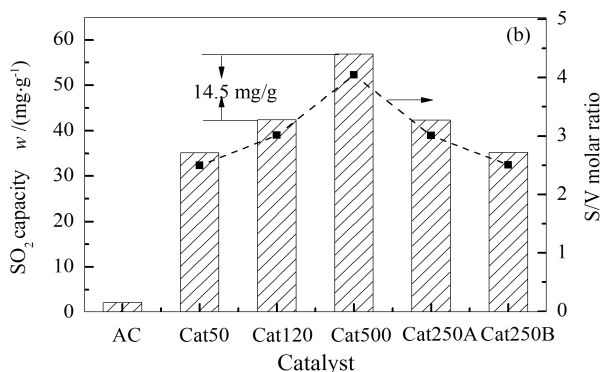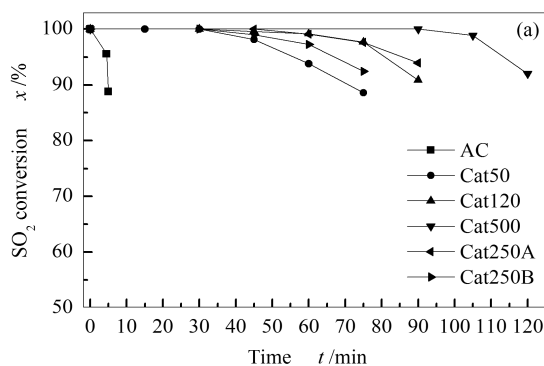

Figure 2   Desulfurization measurement results
reaction conditions：3 g Cat; 0.15% SO_2; 4.5% O_2; 2.5% H_2O; N_2 balance; 4 000 h^{-1}; 120 ℃

    Since the catalyst could be activated at low temperatures, further calcination becomes an unnecessary procedure. However, the subsequent calcination at 500 ℃ in nitrogen, during which the

$VOSO_4$ impregnated is decomposed, indeed increases SO_2 retention. As noted previously, there was 3.53% $VOSO_4$ initially impregnated in fresh Cat120, in which the sulfur content corresponds to SO_2 retention

of 14. 1 mg/g. Interestingly, the increscent part of SO_2 retention on Cat500 is 14. 5 mg/g, which is almost equal to the sulfur content in fresh Cat120. In other words, the total sulfur content in Cat120 is equal to that in Cat500 after desulfurization. This result seems to suggest that the increase in SO_2 retention on Cat500 compared to that on Cat120 is not due to further activation of catalyst, but derives from decomposition of $VOSO_4$, which increases pores for sulfate storage.

Additionally, considering the +4 oxidation state of vanadium in $VOSO_4$ and that calcination was carried out in an inert atmosphere, further preoxidation in air at 250 ℃ was carried out on Cat500 in order to obtain fully oxidized vanadium species, which is expected to be favorable for SO_2 oxidation and hence SO_2 retention. However, the preoxidation exhibits negative effect because SO_2 retention on Cat250A and B is lower than that on Cat500. Moreover, longer preoxidation time results in deeper decrease in SO_2 retention.

Finally, it should be noticed that the molar ratios of SO_2 removed to vanadium of all catalysts are greater than unit, indicating that carbon support is involved in SO_2 adsorption. Furthermore, when GHSV decreases to 400 h^{-1} with the other conditions unchanged, Cat120 and Cat500 exhibit SO_2 retention of about 160 and 180 mg/g with corresponding S/V molar ratios of 11 and 13, respectively, showing that sulfur-containing species formed on catalysts is mainly linked to carbon support. This result is substantially different from that obtained on CuO/AC for SO_2 removal. Tseng et al[7] proposed that CuO/AC exhibits catalytic activity for SO_2 oxidation to SO_3 in temperature range of 100 ~ 250 ℃. The SO_3 formed further reacts with copper oxide to form a sulfate linked to copper without desorption to the gas phase[7]. As a result, $CuSO_4$ is the sulfur-containing species formed, and thus S/Cu molar ratio is not greater than unit[7]. The high S/V molar ratios of sulfated Cat120 and Cat500 show much higher specific activity per mol of V than that of Cu, indicating that SO_2 removal on the catalysts studied is achieved via a different mechanism as compared to that on CuO/AC.

Conclusively, SO_2 retention on AC is greatly enhanced by loading vanadium using vanadyl sulfate as precursor. However, the catalysts exhibit some unexpected properties including activation at low temperatures, opposite effects of calcination and preoxidation on SO_2 retention, and high S/V molar ratio. To understand these, detailed characterizations

are illustrated below.

2.3   Catalyst characterizations

2.3.1   Determination of vanadium oxidation state

An important parameter reflecting the catalytic activity of vanadium based catalyst is the average vanadium oxidation state (V_{os})[17]. Figure 3 shows core level V $2p$ spectra of catalysts. The V $2p_{3/2}$ spectrum of Cat50 splits into two peaks at 517. 4 and 516. 5 eV, which could be assigned to V^{5+} and V^{4+}, respectively[18,19]. The spectrum is thus fitted with these two components. After further treatment at 120 ℃ in air, the peak at 516. 5 eV shifts to higher binding energy while that at 517. 4 eV becomes weaker. This is not surprising because the V^{4+} species become more oxidized while part of the V^{5+} species are reduced by carbon at higher temperature. Carbon is an electron donor, and thereby spurs the peak position of V^{5+} move towards lower binding energy. Thus, it could be considered that two types of V^{5+} species exist in Cat120. $V^{5+}(R)$ represents V^{5+} species reduced by carbon with V $2p_{3/2}$ peak at 517. 0 eV while $V^{5+}(O)$ represents that at 517. 4 eV[18,20]. In this case, the V $2p_{3/2}$ spectrum of Cat120 could be fitted to three components assigned to V^{4+}, $V^{5+}(R)$ and $V^{5+}(O)$, respectively. These results clearly show that the $V^{IV}OSO_4$ impregnated on AC can be easily oxidized into vanadium(V) sulfate phase by oxygen during drying in air, for which the possible candidate is divanadium(V) trioxide disulfate ($V_2^V O_3(SO_4)_2$), which is formed according to the following reaction:

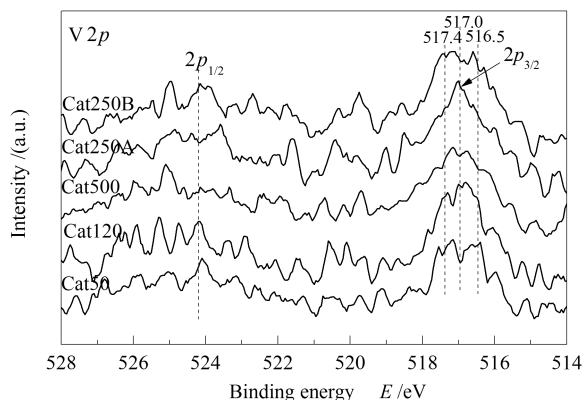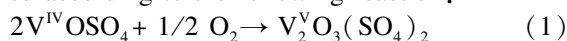$$2V^{IV}OSO_4 + 1/2\ O_2 \rightarrow V_2^V O_3(SO_4)_2 \qquad (1)$$

Figure 3   Core level V $2p$ spectra of the catalysts

It is this vanadium(V) sulfate compound, which can catalyze SO_2 oxidation, results in activation of Cat50 and Cat120. Higher temperature is favorable for deeper oxidation and hence higher SO_2 retention. Actually, the catalytic role of vanadium(V) sulfate

compounds for SO_2 oxidation into SO_3 is well established in sulfuric acid production process[21~23]. In $M_2S_2O_7$-M_2SO_4-V_2O_5/O_2-SO_2-SO_3-N_2 system (M = Na, K, Rb, Cs), the active phase is a molten salt where vanadium oxosulfato complexes are formed at temperatures higher than 420 ℃. V(V) complexes of this type, especially the dimmer $(V^VO)_2O(SO_4)_4^{4-}$, are regarded as catalytic active species[21~23]. Although SO_2 removal on carbon-supported vanadium catalyst was studied extensively, the active component is always considered as vanadium(V) oxide and the catalytic role of vanadium(V) sulfate compounds on AC for SO_2 oxidation at low temperatures has not been reported previously. Clearly, Cat50 and Cat120 represent a new type of carbon-support vanadium catalyst with the vanadium(V) sulfate (possibly $V_2^VO_3(SO_4)_2$) as active component.

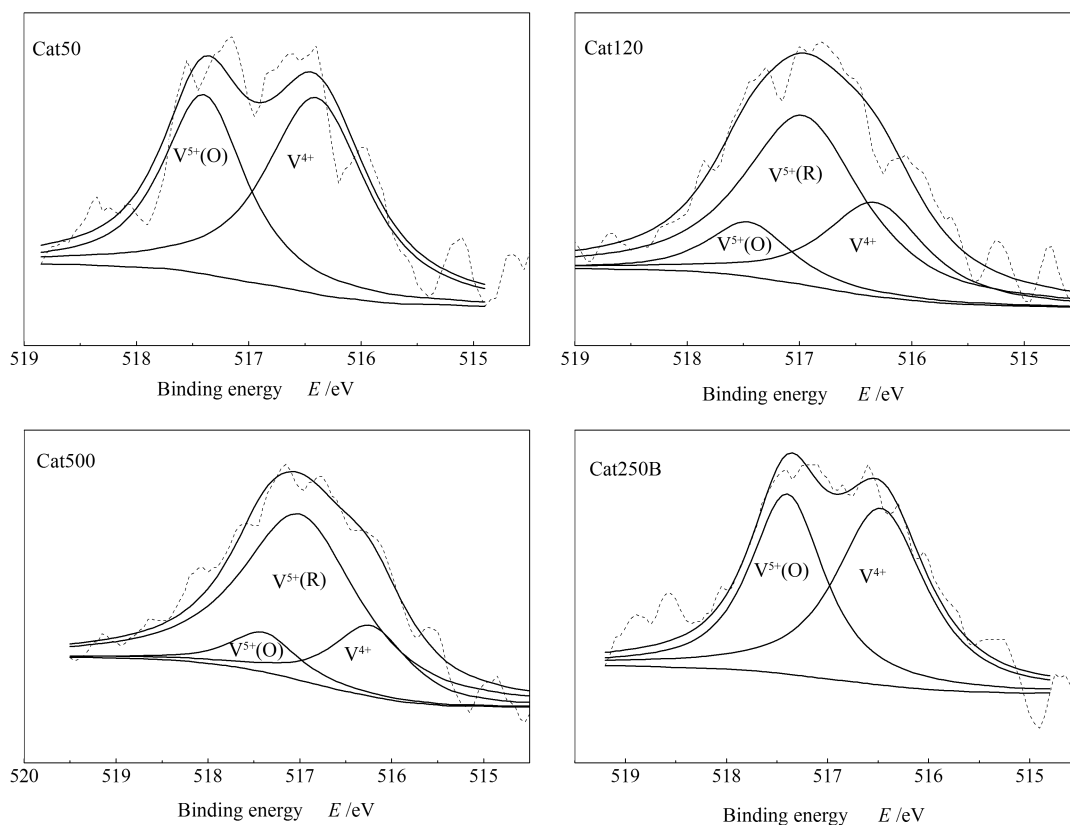Figure 4　Core level V $2p_{3/2}$ spectra and the resulting peaks from the cure fitting

Table 2　Peak position, FWHM, relative abundance and average vanadium oxidation state (V_{os}) deduced from curve fitting of V $2p_{3/2}$ core level

Catalyst	BE /eV			FWHM /eV			Relative abundance			V_{os}
	$V^{5+}(O)$	$V^{5+}(R)$	V^{4+}	$V^{5+}(O)$	$V^{5+}(R)$	V^{4+}	$V^{5+}(O)$	$V^{5+}(R)$	V^{4+}	
Cat50	517.40	–	516.50	0.87	–	1.07	0.43	–	0.57	4.43
Cat120	517.45	516.97	516.33	0.87	1.26	1.07	0.13	0.59	0.28	4.72
Cat500	517.40	517.00	516.30	0.87	1.28	1.00	0.10	0.70	0.20	4.80
Cat250A	–	517.00	–	–	1.26	–	–	1.00	–	5.00
Cat250B	517.40	–	516.44	0.87	–	1.07	0.45	–	0.55	4.45

Upon calcination at 500 ℃ in nitrogen, the vanadium(V) sulfate compound is decomposed forming vanadium(V) oxide. Therefore, the active component in Cat500 is vanadium(V) oxide, V_2O_5. Cat500 can thus be denoted as V_2O_5/AC, representative of traditional carbon-supported vanadium oxide catalyst. The V $2p_{3/2}$ spectrum of Cat500 shows a single wide peak at 517.0 eV, indicating formation of the V^{5+}(R), which is consistent with literature[20]. The V^{5+} species is deeply reduced by carbon at high temperature and hence shows lower binding energy than that in pure V_2O_5. However, the fairly large FWHM (2.21 eV) and the obvious asymmetry should be correlated to large

values of binding energy difference. This is not unexpected since the vanadium species in Cat120 is not fully oxidized and the calcination is carried out in an inert atmosphere. Based on these, the V $2p_{3/2}$ spectrum of Cat500 is fitted to three components at 517. 4, 517. 0 and 516. 5 eV, which are assigned to $V^{5+}(O)$, $V^{5+}(R)$ and V^{4+}, respectively. This result suggests necessity of further preoxidation to obtain fully oxidized vanadium (V) species. After preoxidation in air, Cat250A shows a single symmetry peak at 517. 0 eV with smaller FWHM (1. 23) compared to that of Cat500, indicating formation of more oxidized vanadium (V) oxides. The V $2p_{3/2}$ spectrum of Cat250A is thereby fitted to a single peak at 517. 0 eV. However, when preoxidation time increases to 5h, the vanadium becomes more reduced as V $2p_{3/2}$ spectrum splits into two peaks at 517. 4 eV and 516. 5 eV assigning to V^{5+} (O) and V^{4+}, respectively. The peak-fitting is thereby similar to that of Cat50. It is not easy to interpret this phenomenon. As expected, oxidation by oxygen and reduction by carbon simultaneously occur for vanadium during preoxidation. It seems that oxidation is the main process during first 3 h and then reduction becomes more important in remaining time.

Based on the results above, curve fitting procedure has been performed. Detailed fitting results are listed in Figure 4 and Table 2. The V_{os} is obtained with the relative abundance of different vanadium oxidation states. The vanadium species in Cat250A is considered to be fully oxidized with V_{os} = 5. 00. As seen from Table 2, the V_{os} of the catalysts follows the sequence of Cat50 < Cat250B < Cat120 < Cat500 < Cat250A. Accordingly, a fairly well correlation is established between V_{os} and SO_2 retention except for Cat250A. To a certain extent, this result suggests that deeper vanadium oxidation state reflects higher catalytic activity, resulting in higher SO_2 retention. However, the exception of Cat250A indicates that additional factors must be taken into account.

2.3.2 Study of surface chemistry

Numerous studies demonstrated that surface oxygen functional groups that are readily formed during oxidation in air greatly affect adsorptive properties of carbonaceous materials[24~27]. Figure 5 shows core level O $1s$ spectra. The broad O $1s$ peak observed in binding energy ranging from 529 to 538 eV can be attributed to several oxygen-based surface complexes having different binding energies. As expected, the main oxygen complexes on catalysts surface are metal oxides (oxides of V, Si, Al and Fe etc. existing in carbon matrix) and oxygen functional groups. Meanwhile, there is also sulfate species in Cat50 and Cat120. The binding energies of O $1s$ for

metal oxides, sulfate and oxygen functional groups are in the range of 529. 3 ~ 531. 6, 532 ~ 533 and 531 ~ 536 eV, respectively[28,29]. Therefore, O $1s$ spectra are mainly assigned to oxygen functional groups since the main peaks locate at over 533 eV.
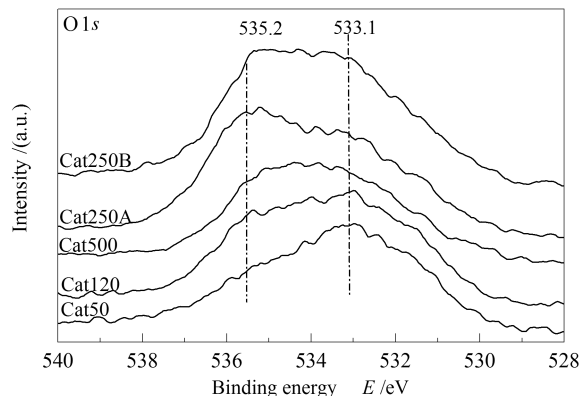

Figure 5   Core level O $1s$ spectra of the catalysts

Table 3   Elemental analysis of catalysts

Catalyst	$w/\%$				
	C	H	O	N	S
Cat500	72. 74	1. 86	4. 11	0. 38	0. 49
Cat250A	70. 51	1. 83	6. 83	0. 36	0. 44
Cat250B	70. 23	1. 43	6. 96	0. 41	0. 48

The binding energy of O $1s$ peaks for Cat50 and Cat120 are about 533. 1 eV, representative of oxygen atoms in sulfate and ester-type groups[28,29]. Further thermal treatment results in an opposite asymmetry of O $1s$ spectrum of Cat500 and a decrease in peak intensity compared to that of Cat120, which is mainly due to the decomposition of vanadium (V) sulfate. More pronounced change is observed after preoxidation in air. The O $1s$ spectra of Cat250A and B show main peaks at 535. 2 eV accompanied with an increase in intensity as compared to that of Cat500, indicating oxidation of carbon surface resulting in formation of carbonyl, carboxyl and/or chemisorbed oxygen as new surface oxygen complexes[29,30]. Further evidence for carbon surface oxidation is provided by elemental analysis. Table 3 gives the C, H, O, N and S contents of Cat500, Cat250A and B. The relatively higher oxygen and lower carbon content of Cat250A and B compared to those of Cat500 indicates bonding of oxygen on carbon surface produced by preoxidation, supporting oxidation of carbon surface.

In a general way, SO_2 retention on carbonaceous materials decreases with increase in oxygen content because oxygen groups inhibit both SO_2 adsorption and its oxidation to SO_3 through blocking SO_2 access to the active sites[24~27]. It is suggested that the new

generated surface oxygen groups presumably reduce the amount of SO_2 available for oxidation to SO_3 by vanadium species, thus decreasing SO_2 retention on Cat250A compared to that on Cat500. For the same reason, these groups are also responsible for the decrease in SO_2 retention on Cat250B.

2.3.3　Study of physical property

　　To better understand effect of preparation conditions on SO_2 retention, physical property of catalysts was also studied. Figure 6 shows the micropore volume and BET surface as a function of preparation conditions. As seen, curve (a) shows same trend as (b). The higher micropore volume of Cat120 than that of Cat50 resulted from deeper evaporation of water at higher temperature. Decomposition of vanadium (V) sulfate should be responsible for further increase in micropore volume of Cat500 compared to that of Cat120. The lower micropore volume of Cat250B than that of Cat250A is probably a result of ablation of AC during preoxidation. However, if preoxidation time is controlled suitably, the ablation effect can be avoided because Cat250A shows the same textural property as Cat500 and AC.
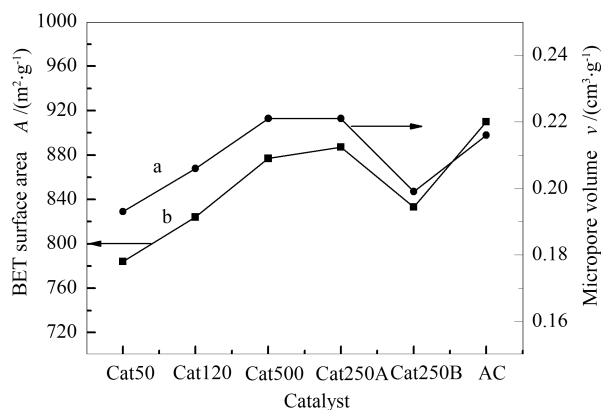

Figure 6　Evolution of the BET
surface area and micropore volume

　　For V_2O_5/AC catalyst, it is generally accepted that after desulfurization H_2SO_4 is the final product, which stores in micorpores[14]. Consequently, higher micorpore volume is expected to be favorable for H_2SO_4 storage and hence higher SO_2 retention. The micropore volume of the catalysts follows a sequence of Cat50 < Cat250B < Cat120 < Cat500 = Cat250A, which could be roughly related to that of SO_2 retention. To some extent, the result shows that higher micropore volume is needed for higher SO_2 retention. However, considering the micropore volume alone cannot interpret lower SO_2 retention on Cat250A than that on Cat500. The evolution of SO_2 retention shown in Figure 2 is a result of

comprehensive effects of preparation conditions on V_{os} and physical-chemical property of catalysts.
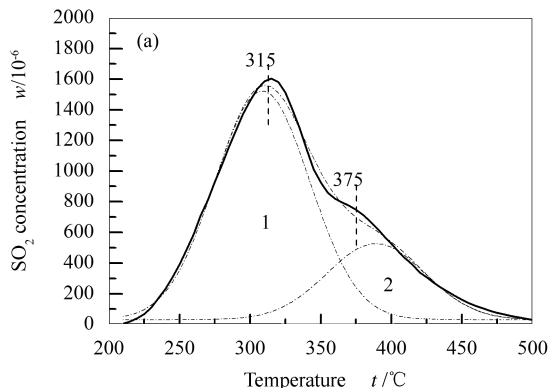
2.3.4　Determination of sulfur-containing species

　　To determine the sulfur-containing species formed, TPD experiments were carried out on used catalysts. Figure 7 shows SO_2-TPD patterns on used Cat120 and Cat500. The results of the other catalysts are similar and not shown for brevity. The SO_2 release occurs in the range of $200 \sim 500\ ℃$ with maximum at $315\ ℃$. Generally, SO_2-TPD patterns on carbonaceous materials after SO_2 adsorption in presence of O_2 show peak at $300 \sim 320\ ℃$[26,31,32], which is related with formation of SO_3 and/or H_2SO_4. Consequently, the main sulfur-containing species formed on catalysts is H_2SO_4 considering presence of H_2O in feed gas.

　　Additionally, it should be noticed that the shoulder at $375\ ℃$ in Figure 7(a) which is caused by decomposition of vanadium (V) sulfate in Cat120. Gauss-fitting shows that the ratio between area 1 and 2 is 2.5, close to molar ratio between H_2SO_4 formed and $VOSO_4$ initially impregnated (2.9), indicating that the vanadium(V) sulfate in Cat120 keeps stable during desulfurization. This is not consistent with the conclusion proposed by Ma et al who suggested that after exposure to O_2/H_2O atmosphere at reaction temperature the $VOSO_4$ preloaded on AC could be readily converted into V_2O_5 and H_2SO_4[13]. To verify this, Cat50 was exposed to O_2/H_2O atmosphere at $120\ ℃$ for 30 min and then TPD experiment was carried out on treated sample. According to the conclusion by Ma et al[13], the SO_2 release should occur in the range $200 \sim 500\ ℃$ with maximum at $315℃$, reflecting decomposition of H_2SO_4. However, the experimental result shows that SO_2 release profile (not shown) is the same as that shown in Figure 1(b), indicating decomposition of $VOSO_4$ initially impregnated, namely vanadium(V) sulfate. These results clearly show that the $VOSO_4$ impregnated on AC cannot be converted into V_2O_5 and H_2SO_4 during desulfurization. Thus, the superior performance of Cat120 for SO_2 removal derives from oxidation of $V^{IV}OSO_4$ into vanadium (V) sulfate, which can act as active component for SO_2 oxidation.

　　Finally, special attention is focused on the shoulder at $\sim 375\ ℃$ in Figure 7(b) although it is not as evident as that in Figure 7(a), indicating existence of vanadium(V) sulfate on used Cat500. Since the vanadium species in fresh Cat500 as representative of traditional V_2O_5/AC is vanadium (V) oxide, the existence of vanadium (V) sulfate on used Cat500

must be a result of reaction between SO_2 and vanadium(V) oxide. In other words, the vanadium (V) oxide in V_2O_5/AC cannot keep stable and most likely transforms into vanadium(V) sulfate during desulfurization. This finding perhaps provides new insight into SO_2 removal behavior of V_2O_5/AC, which will be discussed in detail later.
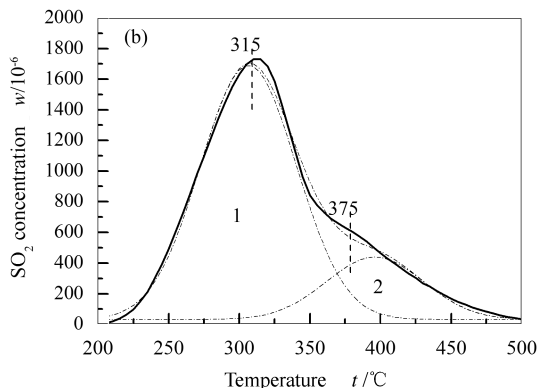

Figure 7   TPD patterns of SO_2 on used Cat120 (a) and Cat500 (b)
experimental conditions: 0.5 g Cat, 400 mL/min N_2, heating rate of 5 ℃/min

Conclusively, the main sulfur-containing species formed on catalysts is H_2SO_4. During desulfurization, vanadium(V) sulfate in Cat120 cannot be converted into V_2O_5 and H_2SO_4, and vanadium(V) oxide in Cat500 is likely transformed into vanadium(V) sulfate.

3   Discussion
3.1   Mechanism for SO_2 catalytic removal

As stated already, the following results have been established: SO_2 removal on AC is greatly enhanced by loading vanadium, which is related with catalytic activity of vanadium for SO_2 oxidation, S/V molar ratio is greater than 1, indicating that one vanadium could catalyze more than one SO_2 oxidation reaction, the reaction product is H_2SO_4, and H_2SO_4 exists on AC support. Accordingly, a mechanism is proposed as follows: SO_2 adsorption, oxidation of SO_2 to SO_3 catalyzed by vanadium in presence of O_2, reaction of SO_3 with H_2O adsorbed to form H_2SO_4 on AC surface, H_2SO_4 is continuously swept from surface to pores by excess water to free active sites, and thus a new catalytic cycle starts again. In the case of SO_2 oxidation, Mars-van Krevelen mechanism is proposed. SO_2 is oxidized to SO_3 by vanadium(V) with parallel reduction of vanadium(V) to vanadium (IV). Vanadium(IV) is reoxidised to vanadium(V) by O_2 accompanied with SO_3 leaving vanadium.

For Cat120, it is no doubt that the vanadium species responsible for SO_2 oxidation into SO_3 and the subsequent H_2SO_4 formation is vanadium(V) sulfate (possibly $V_2^V O_3(SO_4)_2$). For Cat500, which is representative of the traditional V_2O_5/AC, the vanadium species for formation of H_2SO_4 is always considered as the vanadium(V) oxide, V_2O_5[28]. However, the shoulder observed at ~ 375 ℃ in Figure 7(b) suggests the transformation of vanadium (V) oxide into vanadium(V) sulfate. Combined with the catalytic role of vanadium(V) sulfate for SO_2 oxidation as evidenced by the superior performance of Cat120, SO_2 removal on Cat500 likely follows a mechanism that the vanadium(V) oxide transforms into vanadium(V) sulfate and the latter is then responsible for subsequent SO_2 oxidation into H_2SO_4. Using this hypothesis the key difference between CuO/AC and V_2O_5/AC for SO_2 removal can be found. Although copper(II) oxide is active for SO_2 oxidation, the transformation of copper(II) oxide into copper(II) sulfate greatly deactivates CuO/AC catalyst because copper(II) sulfate is inactive for catalytic reaction especially at low temperature[33,34]. Therefore, it is expected that there is no H_2SO_4 formation benefited from the catalytic activity of copper species, leading to the fact that $CuSO_4$ is the only sulfur-containing species formed on catalyst after desulfurization and thus S/Cu molar ratio is not greater than unit. In contrast, for $V_2O_5/$ AC, such a transformation of vanadium(V) oxide into vanadium(V) sulfate does not deactivate catalyst. The vanadium(V) sulfate could further catalyze SO_2 oxidation into SO_3, leading to H_2SO_4 formation and high specific activity per mole of V, namely high S/V molar ratio.

A literature survey shows that SO_2 oxidation over carbon-supported vanadium catalyst is studied extensively[13,14,20,28,35,36]. However, all of the authors agree that the vanadium species for SO_2 oxidation into

H_2SO_4 or SO_3 existed on carbon surface is vanadium (Ⅴ) oxide and the chemical form vanadium (Ⅴ) oxide is not changed during SO_2 oxidation. Although Ma et al[13] suggests formation of $VOSO_4$-like species, $VOSO_4$-like species is considered as intermediate, which readily converts into V_2O_5 and H_2SO_4 during desulfurization. In present study, the probability of transformation of vanadium (Ⅴ) oxide into vanadium (Ⅴ) sulfate is proposed. More importantly, the catalytic role of vanadium (Ⅴ) sulfate for SO_2 oxidation on AC at low temperature is established. Actually, the molecular structure change of vanadium species in V_2O_5-Cs_2SO_4/SiO_2 catalyst for sulfuric production is well demonstrated[21]. During calcination the vanadium dissolved in a sulfate molten salt predominantly in the form of mononuclear $V^VO_2(SO_4)_2^{3-}$ molten oxosulfato complex. Exposure of the catalyst to SO_2/O_2/N_2 mixture results in uptake of SO_3 and the transformation of $V^VO_2(SO_4)_2^{3-}$ into a pyrosulfate molten salt, in which vanadium occurs predominantly in the form of the binuclear $(V^VO)_2O(SO_4)_4^{4-}$, which is considered as active species responsible sulfuric production[21]. A molecular structure change of vanadium species in V_2O_5/AC catalyst also likely exists during SO_2 oxidation. The SO_2 is oxidized into SO_3 catalyzed by vanadium (Ⅴ) oxide and after uptake SO_3 the vanadium(Ⅴ) oxide transformed into vanadium(Ⅴ) sulfate. During the subsequent SO_2 oxidation process, the vanadium (Ⅴ) sulfate keeps stable and is responsible for SO_2 oxidation into SO_3 which then reacts with H_2O to form H_2SO_4. However, the accurate chemical form of vanadium(Ⅴ) sulfate in Cat120 should be further determined. More specific and accurate studies will be carried out in forthcoming research.

3.2　Factors influencing SO_2 retention

To better illustrate effect of preparation conditions, dependence of SO_2 retention on V_{os} and physical-chemical property of catalyst is analyzed comprehensively in this section. Drying at 120 ℃ results in more complete oxidation of $V^{IV}OSO_4$ into the vanadium(Ⅴ) sulfate favorable for SO_2 oxidation and higher micropore volume suitable for H_2SO_4 storage than that at 50 ℃, leading to higher SO_2 retention on Cat120 than that on Cat50. Due to formation of surface oxygen groups, preoxidation decreases SO_2 retention on Cat250A than that on Cat500 although the vanadium species in Cat250A is more oxidized than that in Cat500. Increasing

preoxidation time results in ablation of carbon support and reduction of vanadium, decreasing SO_2 retention on Cat250A compared to that on Cat250B. However, considering the different active components, it should be more discreet to understand the increase in SO_2 retention on Cat500 than that on Cat120.

Curve-fitting of XPS shows that V_{os} of Cat120 is 4.72 while that of Cat500 is 4.80, suggesting that the catalytic activity of vanadium is not significantly improved during calcination. Additionally, calcination at 500 ℃ in nitrogen is expected to generate two main changes in physical-chemical property of catalyst. On one hand, reduction of sulfate (SO_4^{2-}) to SO_2 leaves oxygen over carbon surface that produces oxygen functional groups. On the other hand, the micropore volume is increased as a result of decomposition of vanadium(Ⅴ) sulfate. As discussed previously, the increase in oxygen groups is negative for SO_2 retention, whereas the increased micropore volume has positive effect. Therefore, the increase in SO_2 retention on Cat500 compared to that on Cat120 should be mainly attributed to the increase in micropore volume, which is suitable for sulfate storage.

4　Conclusions

Vanadyl sulfate ($V^{IV}OSO_4$) is used to prepare carbon-supported vanadium catalyst for flue gas desulfurization. The $V^{IV}OSO_4$ impregnated on AC is easily oxidized into vanadium (Ⅴ) sulfate phase (possibly $V_2O_3(SO_4)_2$) during drying in air, which exhibits high catalytic activity toward SO_2 oxidation. Higher temperature is favorable for more complete oxidation of $V^{IV}OSO_4$ into the vanadium(Ⅴ) sulfate and thus higher SO_2 retention. The vanadium (Ⅴ) sulfate could be decomposed upon calcination in nitrogen with optimum temperature of 500 ℃ to form vanadium(Ⅴ) oxide, improving SO_2 retention due to increase in micorpore volume suitable for H_2SO_4 storage. After calcination, the subsequent preoxidation in air produces negative effect on SO_2 retention due to ablation of carbon support, reduction of vanadium and/or formation of surface oxygen groups. Additionally, this paper provides preliminary evidence for the transformation of vanadium (Ⅴ) oxide in V_2O_5/AC into vanadium (Ⅴ) sulfate, indicating that the mechanism of SO_2 removal on V_2O_5/AC likely follows the mechanism that the vanadium(Ⅴ) oxide transforms into vanadium(Ⅴ) sulfate and the latter is then responsible for subsequent SO_2 oxidation into H_2SO_4.

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利用硫酸氧钒制备钒炭催化剂用于烟气脱硫

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摘 要：利用硫酸氧钒制备钒炭催化剂用于烟气脱硫。研究发现,负载在活性炭上的硫酸氧钒极易被氧化为五价钒硫酸盐,这些五价钒硫酸盐具有很高的氧化 SO_2 的活性,极大地促进了 SO_2 在活性炭上的脱除。而且,通过煅烧可以将五价钒硫酸盐分解为五价钒氧化物,最佳煅烧温度为 500℃,由于煅烧后用于储存硫酸的微孔孔容增加, SO_2 的吸附容量得到了进一步提高,由此表明,利用硫酸氧钒可以制备传统的 V_2O_5/AC 催化剂。为了获得完全氧化的钒物种,对煅烧后的催化剂进行了空气中预氧化,但由于含氧官能团的形成、炭载体的烧蚀以及钒的还原,预氧化不利于脱硫。此外,研究中得到初步证据证明脱硫过程中 V_2O_5/AC 催化剂中五价钒氧化物转变成了五价钒硫酸盐,结合五价钒硫酸盐所表现出的氧化 SO_2 的能力,推测 SO_2 在 V_2O_5/AC 上的脱除遵循以下机理：五价钒氧化物先转变为五价钒硫酸盐,后者催化氧化 SO_2 为硫酸。

关键词： V_2O_5/AC；脱硫；硫酸钒；催化作用；低温