Available online at www.sciencedirect.com

ScienceDirect

Catalysis Today 131 (2008) 322–329

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Regeneration of a vanadium pentoxide supported activated coke catalyst-sorbent used in simultaneous sulfur dioxide and nitric oxide removal from flue gas: Effect of ammonia

Yanxia Guo [a,b], Zhenyu Liu [a,c,*], Qingya Liu [c], Zhanggen Huang [a]

[a] *State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, China*
[b] *Graduate School of the Chinese Academy of Sciences, Beijing 100039, China*
[c] *State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, China*

Abstract

A vanadium pentoxide supported activated coke (V_2O_5/AC) catalyst-sorbent has been reported to be very active for simultaneous removal of SO_2 and NO under dry conditions at temperatures of 200 °C and below. Regeneration of the SO_2-captured catalyst-sorbent is a key step in operation of such a process, which influences the catalyst-sorbent's SO_2 and NO removal activities, lifetime, as well as recovery of sulfur. Due to limited information in this regard, this paper studies thermal regeneration of a V_2O_5/AC catalyst-sorbent with emphases on the effect of atmosphere. The optimum regeneration temperature is found to be 380 °C in an Ar stream and 300 °C in a 5% NH_3/Ar stream. Compared to the fresh V_2O_5/AC, the V_2O_5/ACs regenerated in Ar show lower SO_2 adsorption capacities and higher NO removal activities, while the regenerated V_2O_5/ACs by 5% NH_3/Ar show higher and stable SO_2 adsorption capacities and higher NO removal activities. Two types of reactions occur during the regeneration: reduction of the adsorbed sulfur species by carbon to SO_2 and CO_2, and oxidation of carbon by oxygen in the V_2O_5/AC to CO_2. The carbon consumption of the latter is much more than that of the former in an Ar atmosphere, but fully suppressed by the presence of 5% NH_3. Detailed analysis and characterization of the V_2O_5/AC subjected to the regenerations are presented.

Keywords: V_2O_5/AC; SO_2 and NO removal; Regeneration; NH_3; Carbon burning-off

1. Introduction

SO_2 and NO in flue gas are major air pollutants responsible for acid rain and photochemical smog. Many techniques have been developed to suppress their emissions but most of them are capable of treating only one of them. Some catalyst-sorbent based techniques are advantageous due to their ability to remove SO_2 and NO simultaneously under dry conditions. In these technologies, SO_2 is removed through chemical adsorption to form sulfates or H_2SO_4 and NO is removed through reduction by a reducing reagent to form N_2. Chemical adsorption of SO_2, however, implies that the catalyst-sorbent has to be regenerated periodically upon saturation of adsorbed sulfur species.

Many catalyst-sorbents have been studied for SO_2 and NO removal, including those based on CuO/Al_2O_3 and those based on activated carbon/coke (AC) [1–5]. The AC-based catalyst-sorbents are advantageous due to its high activities at flue gas temperatures (120–250 °C). A successful example is the Mitsui-BF process [6–8], which uses a coal-derived AC as catalyst-sorbent and operates at about 150 °C for SO_2 and NO removal. The used ACs are then regenerated to recover their activity by an inert atmosphere at 400 °C and the concentrated SO_2 produced in this process is treated in another unit for H_2SO_4 production. It is no doubt that the addition of a separated unit for H_2SO_4 production complicates the overall SO_2 removal system.

Our recent studies [9–11] show that (1) modification of AC by V_2O_5 yields a catalyst-sorbent (termed V_2O_5/AC) of higher activities for both SO_2 removal and selective catalytic reduction (SCR) of NO; (2) the used or "SO_2-captured" V_2O_5/AC can be

---

* Corresponding author at: State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, China. Tel.: +86 351 405 3091; fax: +86 351 405 3091.
E-mail address: zyl@public.ty.sx.cn (Z. Liu).

0920-5861/$ – see front matter © 2008 Published by Elsevier B.V.
doi:10.1016/j.cattod.2007.10.032

regenerated in a NH_3-containning atmosphere at temperatures lower than that used in Mitsui-BF process; (3) the presence of NH_3 during regeneration significantly promoted V_2O_5/AC's activities in the subsequent SO_2 and NO removal process; (4) solid ammonium–sulfur salts can be obtained directly upon cooling of the regeneration effluent, which eliminates the request for additional units for on-site conversion of gaseous SO_2 to H_2SO_4.

It is generally accepted that, for AC-based catalyst-sorbents, the SO_2 removal process mainly consists of oxidation of SO_2 to SO_3 followed by a reaction of SO_3 with H_2O to H_2SO_4 [12], and the regeneration process mainly involves reduction of H_2SO_4 to concentrated SO_2[6]. However, the improved activities after the regeneration process, especially in NH_3-containning atmosphere, suggest that other important reactions may also occur during the regeneration, which results in permanent changes in the catalyst-sorbent's physical and chemical properties. Information in this regard is rather limited in the literature and is of importance to understand the nature of the regeneration, to control carbon consumption in catalyst-sorbent, and to optimize the regeneration conditions.

In this paper, regeneration of a used V_2O_5/AC is studied in Ar in the absence or presence of 5% NH_3 to elucidate effect of NH_3 on changes in physical and chemical properties of the catalyst-sorbent. The information obtained is important not only to V_2O_5/AC but also to other types of AC-based catalyst-sorbents.

2. Experimental

2.1. Preparation of V_2O_5/AC catalyst-sorbent

A coal-derived commercial granule AC from Xinhua Chemical Plant (Taiyuan, China) with particle sizes of 30–60 meshes (0.23–0.45 mm) was used. The V_2O_5/AC was prepared by pore volume impregnation using an aqueous solution containing ammonium metavanadate and oxalic acid. After the impregnation, the samples were dried at 110 °C for 5 h, followed by calcination in Ar at 500 °C for 5 h and pre-oxidation in air at 250 °C for 5 h. The V_2O_5 loading of the V_2O_5/AC is 2 wt%. For convenience, the catalyst-sorbent is denoted V/AC in general, the fresh sample is denoted V/AC-F, and the used or "SO_2-captured" sample is denoted V/AC-S in this paper.

2.2. Activity test and regeneration

Simultaneous SO_2 and NO removal experiments were performed in a fixed-bed reactor of 12 mm in diameter at 200 °C. The feed gas contains 1500 ppm SO_2, 500 ppm NO, 500 ppm NH_3, 5% O_2, 2% H_2O and balance Ar. The space velocity was 7800 h^{-1}. Concentrations of SO_2, NO and O_2 in the inlet and the outlet of the reactor were measured on-line by a Flue Gas Analyzer (KM9106). SO_2 removal efficiency of the V/AC was 100% initially but decreased with time on stream after a breakthrough in effluent SO_2 concentration. When the SO_2 removal efficiency decreased to 80%, the mass of SO_2 captured on the V/AC was calculated and termed SO_2 capture capacity (SC_{80} in short, mg/g). The used V/AC was then in situ regenerated in an Ar or 5% NH_3 in Ar (termed 5% NH_3/Ar) stream at a flow rate of 100 ml/min and a temperature of 250–400 °C for 1 h. Afterwards, the V/AC was cooled to 200 °C with Ar purge for the next SO_2/NO removal-regeneration cycle. The regenerated V/AC samples are termed NH_3-*T*-*n* or Ar-*T*-*n*, where *T* denotes the regeneration temperature and *n* denotes the number of SO_2/NO removal-regeneration cycles.

2.3. Characterization of V/AC

Temperature programmed experiments were performed in another fixed-bed reactor of 6 mm in diameter with a sample loading of 0.2 g and a gas flow rate of 100 ml/min. After being purged in an Ar flow at 100 °C for 30 min, the V/AC-S was heated up at a rate of 10 °C/min in an Ar or a 5% NH_3/Ar stream. The effluent gas was analyzed on-line by a mass spectrometer (Balzers, Omnistar200).

Contents of C, N and S of the V/AC samples were measured on a Vario EL Analyzer of Elementar Analysensysteme GmbH Co. BET surface area and pore volume of the samples were determined through nitrogen adsorption at 77 K on an ASAP2000 analyzer.

Surface acidity of the V/AC samples was estimated by acid–base titration, through mixing of 1 g V/AC with a NaOH solution (25 ml, 0.1 mol/l) at the ambient temperature for 96 h, filtration of the mixture to obtain a filtrate, addition of a HCl solution (25 ml, 0.1 mol/l) to the filtrate, and titration of the solution with a NaOH solution (0.1 mol/l) with a phenolphthalein as indicator.

3. Results and discussion

3.1. Activities of the V/AC regenerated in Ar or 5% NH_3/Ar

3.1.1. Effect of regeneration temperature

Fig. 1 shows V/AC's SO_2 and NO conversions at 200 °C after it has been regenerated once in Ar at various temperatures. Compared to V/AC-F, all the Ar-regenerated V/AC samples show lower SO_2 conversions. Among them, the ones regenerated at 350 and 380 °C show relatively higher SO_2 removal activities with breakthrough time of about 40 min, about 20% shorter than that of V/AC-F, while the ones regenerated at 300 and 400 °C show lower SO_2 removal activities. NO conversions of all the Ar-regenerated V/AC samples, however, are higher than that of V/AC-F, with maximums of about 70% for V/ACs regenerated at 350 and 380 °C. Apparently, the SO_2-adsorbed V/AC (V/AC-S) can be reasonably regenerated in Ar, and a temperature in a range of 350–380 °C is optimal.

Fig. 2 shows SO_2 and NO conversions at 200 °C of V/AC sample regenerated once in 5% NH_3/Ar at various temperatures. The V/AC regenerated at 280 °C (NH_3-280-1) shows the lowest SO_2 conversion with a breakthrough time of 40 min, which is similar to that of Ar-380-1, the highest in Ar-regeneration (Fig. 1). The V/AC samples regenerated at 300 and 400 °C shows SO_2 breakthrough time of about 50 min, which is similar to that of V/AC-F. The V/AC regenerated at

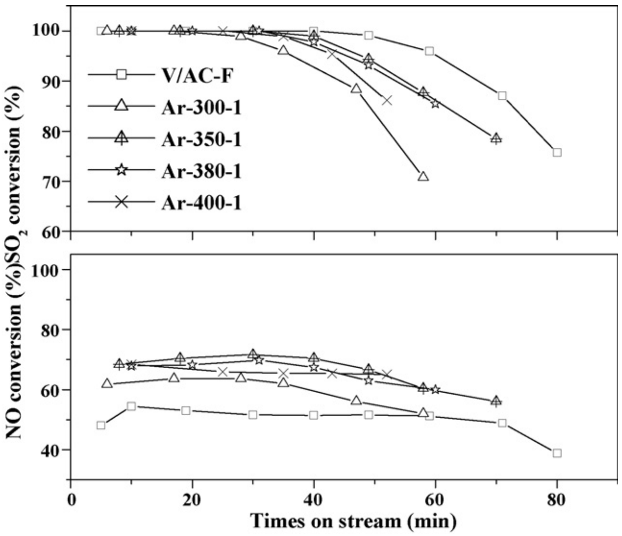

Fig. 1. Simultaneous SO_2 and NO removal at 200 °C over V/ACs regenerated in Ar at various temperatures.

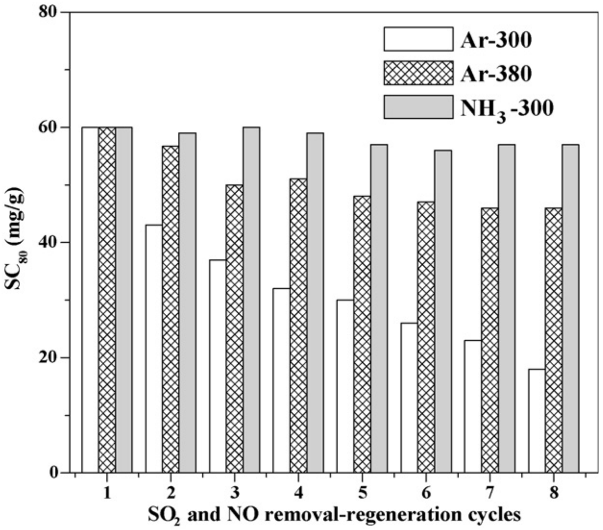

Fig. 3. SO_2 capture capacity of V/AC during consecutive SO_2/NO removal-regeneration cycles.

350 °C shows the longest breakthrough time of 60 min, about 20% longer than that of V/AC-F. Similar to the V/AC samples regenerated in Ar, those regenerated in 5% NH_3/Ar also show higher NO conversions, compared to V/AC-F. However, their initial NO conversions are much higher. The NO conversions are initially 100% for the V/AC samples regenerated at 280 and 300 °C and decrease to 70% when SO_2 conversions decrease to 80%. Clearly, the presence of 5% NH_3 in Ar significantly promotes the V/AC's SO_2 and NO removal activities and lowers its regeneration temperature in comparison to the regeneration in Ar. The optimum temperature seems to be 300 °C for regeneration in 5% NH_3/Ar.

3.1.2. Activity of V/AC in consecutive SO_2/NO removal-regeneration cycles

Differences in SO_2 and NO removal activities between the V/AC samples regenerated in Ar and in 5% NH_3/Ar may become more pronounced if the samples are subjected to consecutive SO_2/NO removal-regeneration cycles. Fig. 3 shows SO_2 capture capacities (SC_{80}) of the V/AC samples regenerated at the optimum regeneration temperatures, 380 °C in Ar and 300 °C in 5% NH_3/Ar. SC_{80} of V/AC regenerated in Ar at 300 °C are also presented for comparison. Within 8 consecutive cycles, the regeneration in 5% NH_3/Ar at 300 °C yields a stable SC_{80} of about 57 mg/g. The regeneration in Ar at 380 and 300 °C, however, results in progressive decreases in SC_{80}, with a 22% reduction at 380 °C and a 70% reduction at 300 °C in 8 cycles, in comparison to the initial SC_{80} of 60 mg/g.

Fig. 4 shows NO conversions obtained simultaneously in the consecutive cycles. The V/AC regenerated in 5% NH_3/Ar at 300 °C shows the highest NO conversions, 100% initially and about 70% at a SO_2 conversion of 80%. Within 8 consecutive cycles, the curves of NO conversion do not change much. The

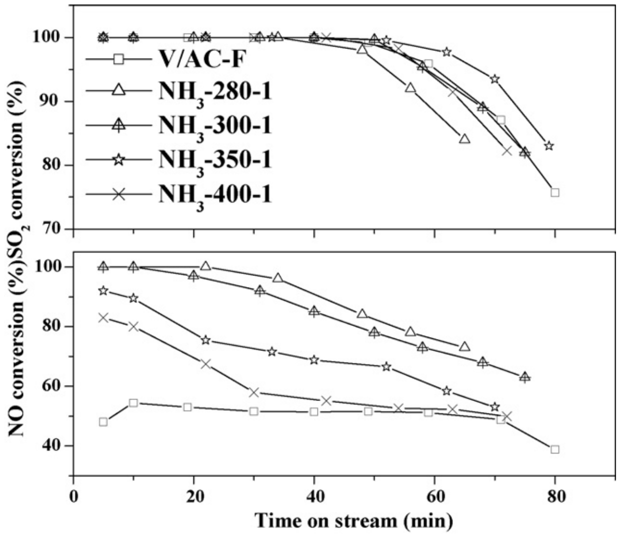

Fig. 2. Simultaneous SO_2 and NO removal at 200 °C over V/ACs regenerated in 5% NH_3/Ar at various temperatures.

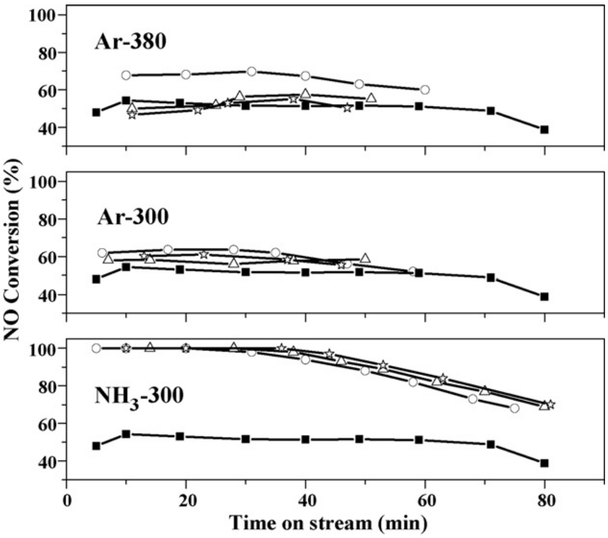

Fig. 4. NO conversions of V/AC during consecutive SO_2/NO removal-regeneration cycles. V/AC-F (■), after cycles 1 (○), 3 (△) and 8 (□).

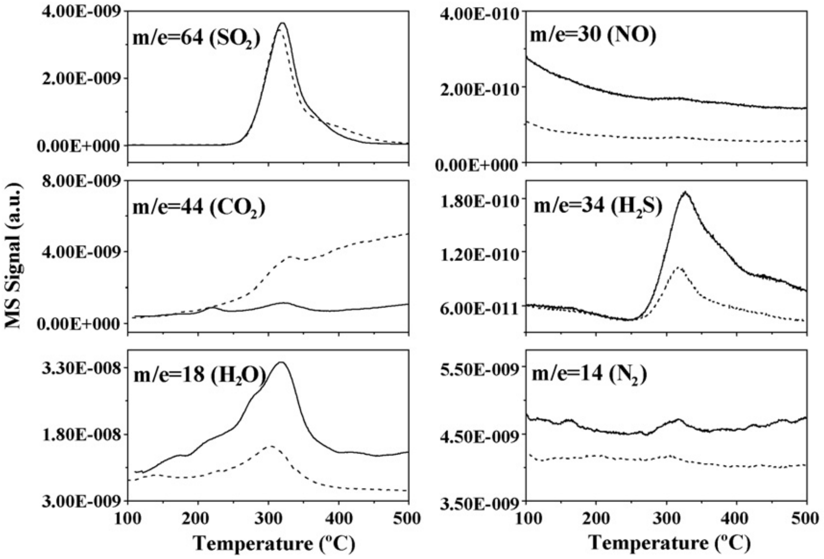

Fig. 5. MS signals of the effluent gases during regeneration of V/AC-S in Mode I in Ar (dot line) or in 5% NH_3/Ar (solid line).

V/AC regenerated in Ar show much lower NO conversions, with a maximum of 60% in 8 cycles.

3.2. SO_2 desorption from V/AC-S and carbon consumption during regeneration

3.2.1. SO_2 desorption behaviors

The data presented above clearly show that the presence of 5% NH_3 in Ar during the regeneration significantly lowers regeneration temperatures and improves V/AC's SO_2 and NO removal activities and long-term stabilities. These improvements may result from changes in SO_2 desorption and/or V/AC's surface properties during the regeneration due to the presence of NH_3. To elucidate these effects, temperature programmed experiments are carried out on V/AC-S in two modes to elucidate SO_2 desorption: from 100 to 500 °C at a heating rate of 10 °C/min in Mode I and from 100 to 300 °C at a heating rate of 10 °C/min and then maintained at 300 °C for 40 min in Mode II.

Fig. 5 shows MS signals of SO_2, CO_2, H_2O, NO, H_2S and N_2 in the effluent obtained in Mode I in an Ar stream (the dot lines) and in a 5% NH_3/Ar stream (the solid lines). It is interesting that the SO_2 desorption behavior in the two cases are identical within experimental error, with one broad peak at 250–400 °C. This suggests that regeneration of the used catalyst-sorbent (actually, reduction of H_2SO_4 to gaseous SO_2 as discussed in the introduction) begins at 250 °C and can be accomplished in a temperature range of 250–400 °C. This also indicates that the presence of NH_3 has no effect on reduction of H_2SO_4. The profiles of other gases, however, are very different in the two cases. In the Ar stream, CO_2 release is quite obvious, which begins at 200 °C and progressively increases with increasing temperature, with a peak at temperatures that SO_2 releases. Additionally, releases of H_2O and H_2S are also observed at temperatures of SO_2 release. These information indicate that the oxygen in the V/AC, such as in the adsorbed SO_2 species (mainly H_2SO_4), and/or in metal oxides, and/or in oxygen-containing functional groups, undergo reactions with carbon to yield CO_2 and with hydrogen to yield H_2O in Ar stream. In contrast, the presence of 5% NH_3 results in much less CO_2 release in the whole temperature range, but more H_2O and H_2S releases and little N_2 release during the SO_2 release. The significant reduction in CO_2 release and obvious increase in H_2S release suggest that NH_3 participates in the reduction of H_2SO_4. The significant increase in H_2O release suggests that hydrogen in NH_3 reacts with oxygen in the V/AC, which may inhibit the reactions between the oxygen and carbon and account for the decreased CO_2 release, especially at the higher temperatures. In other words, the presence of NH_3 in Ar stream may reduce carbon consumption of V/AC. However, it is surprise that the presence of NH_3 results in little changes in releases of N-containing gases in this process, suggesting that nitrogen in NH_3 is mainly transformed to N-containing functional groups on the V/AC surface. This might be one of the reasons for the high SO_2 and NO removal activities after the regeneration, which will be discussed in detail in Section 3.3.

Fig. 6 shows SO_2, CO_2, H_2O, NO, H_2S and N_2 profiles obtained in Mode II. Similar to those observed in Mode I (Fig. 5), the desorption of SO_2 is not affected by the presence of NH_3, but the releases of CO_2, H_2O and H_2S are significantly affected by the presence of NH_3. These further confirm the above conclusions.

3.2.2. Carbon consumption during the regenerations

The above analysis clearly indicate that (1) carbon consumption in V/AC is generalized into two ways: reducing H_2SO_4 and reacting with oxygen in the V/AC; (2) the carbon consumption due to H_2SO_4 reduction is much smaller than that due to reaction with oxygen in the V/AC; (3) NH_3 may suppress the reaction of carbon with oxygen in the V/AC and substitute a portion of carbon for H_2SO_4 reduction.

It is important to point out that carbon loss is always regarded as the major obstacle in application of the AC-based

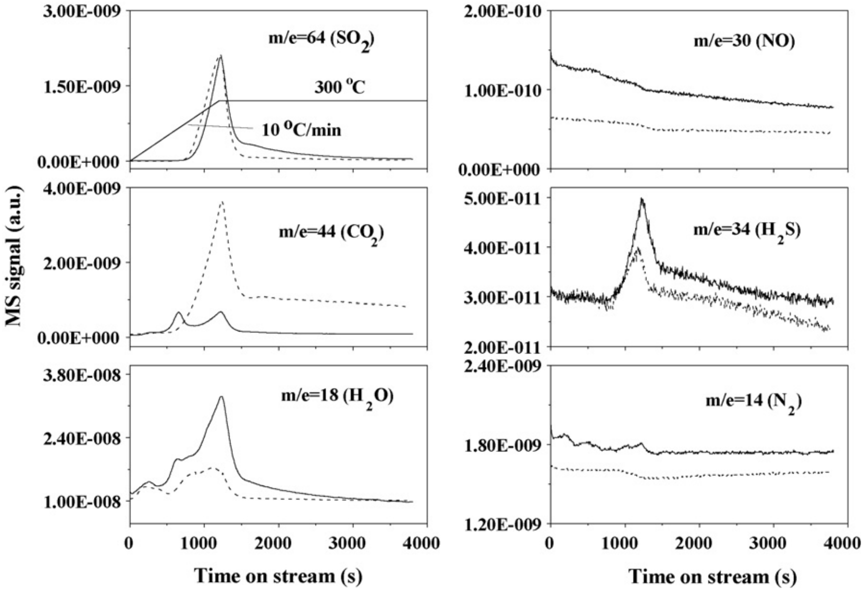

Fig. 6. MS signals of the effluent gases during regeneration of V/AC-S in Mode II in Ar (dot line) or in 5% NH_3/Ar (solid line).

catalyst-sorbent for SO_2 removal when thermal regeneration in an inert atmosphere is employed. The observations in this work reveal that the large carbon consumption encountered in industrial application can be significantly suppressed by addition of a small amount of NH_3 into the inert atmosphere.

3.3. Effect of regeneration on V/AC's properties

3.3.1. Pore structure analysis

Table 1 shows the physical properties and sulfur contents of some of V/AC samples. Compared to the fresh sample V/AC-F, BET surface area and total pore volume of the SO_2-adsorbed sample V/AC-S are 185.8 m^2/g and 0.09 cm^3/g smaller, respectively, and the micro-pore surface area and micro-pore volume of V/AC-S are 165.4 m^2/g and 0.07 cm^3/g smaller, respectively. Clearly, the decreases in surface area and pore volume after SO_2 and NO removal are mainly attributed to loss of micro-pores. This suggests that the sulfur species formed in SO_2 removal stores mainly in the micro-pores, as reported in the literatures [8,13].

After Ar-regeneration at 300 °C, BET surface area and micro-pore surface area of V/AC recover to 759.3 and 507.4 m^2/g, respectively (see Ar-300-1), which are about 10% lower than that of V/AC-F. The losses in total pore and micro-pore volumes are also at the same level. These losses may be attributed to the presence of non-regenerable sulfur in the micro-pores, as indicated by the fact that the sulfur content of Ar-300-1 is higher than that of V/AC-F. The increase of SO_2/NO removal-regeneration cycles further decreases the V/AC's micro-pore surface area and micro-pore volume and increases its sulfur content, as demonstrated by the data of Ar-300-3 and Ar-300-8. These indicate accumulations of non-regenerable sulfur in the micro-pores with increasing SO_2/NO removal-regeneration cycles under the conditions used. However, it is important to note that the losses in micro-pore surface area and micro-pore volume are relatively smaller compared to the losses in SO_2 capture capacity (SC_{80}) in Fig. 3. It is also important to note that the BET surface area and total pore volume of Ar-300-8 are actually higher than that of V/AC-F, indicating widening of meso- and macro-pore and/or formation of new pores during the Ar-regeneration. The meso- and macro-pores play little role in SO_2 removal since decrease in SC_{80} are observed with increases in meso- and macro-pore volume and surface area.

Similar to Ar-regeneration, 5% NH_3/Ar-regeneration also decreases micro-pore surface area and volume (compared to V/

Table 1
Physical properties and sulfur contents of various V/AC samples

Samples	BET surface area ($m^2\,g^{-1}$)	Total volume ($ml\,g^{-1}$)	Micro-pore area ($m^2\,g^{-1}$)	Micro-pore volume ($ml\,g^{-1}$)	Average pore diameter (nm)	Sulfur content (wt%)
V/AC-F	816.5	0.432	561.8	0.242	0.53	0.42
V/AC-S	630.7	0.343	396.4	0.172	0.54	2.49
Ar-300-1	759.3	0.406	507.4	0.219	0.52	0.95
Ar-300-3	780.7	0.431	477.2	0.206	0.53	0.97
Ar-300-8	838.6	0.483	471.9	0.206	0.54	1.31
NH_3-300-1	780.8	0.421	511.8	0.221	0.53	0.86
NH_3-300-3	772.7	0.414	500.5	0.216	0.53	1.11
NH_3-300-8	731.1	0.391	477.3	0.206	0.53	1.71

AC-F) due to presence of residual sulfur after the 5% NH_3/Ar regeneration. The important differences of the two regeneration processes lie in the changes of BET surface area, total pore volume and sulfur content. The V/AC regenerated in 5% NH_3/Ar show decreased BET surface area and total pore volume while V/AC regenerated in Ar show increased ones. More importantly, the sulfur contents in the 5% NH_3/Ar-regenerated V/AC samples are higher than those in Ar-regenerated V/AC samples after the third cycle (Table 1), which is contradictive to their SO_2 removal activities. These indicate that the higher SO_2 and NO removal activities of NH_3-regenerated samples cannot be attributed to the change in micro-pore structure and the residual sulfur after regeneration may have little effect on SO_2 removal activities in the subsequent cycles.

Fig. 7 correlates the V/AC's pore volume with sulfur content. The same linear relationship between the micro-pore volume and the sulfur content for V/AC regenerated in Ar (the filled symbols) and in 5% NH_3/Ar (the open symbols) indicate that the changes in micro-pore volume are caused mainly by the presence of non-regenerable sulfur species. The similar trends of total pore volume and micro-pore volume with respect to sulfur content for V/AC regenerated in 5% NH_3/Ar indicate that the changes in the total pore volume results mainly from the changes in micro-pore volume in the presence of NH_3. The increase in total pore volume with an increase in sulfur content for the Ar-regenerated V/AC is difficult to understand, unless it is attributed to widening of the meso- and macro-pores during the Ar-regeneration.

3.3.2. *Chemical properties of the V/AC*

Although it has shown that the presence of NH_3 during the regeneration reduces V/AC's regeneration temperature and carbon loss and affects V/AC's pore structure, the main reasons responsible for the high SO_2 capture capacity and high NO removal activity are still not clear. The V/AC's surface chemical properties are analyzed and correlated to the SO_2 and NO removal activities to elucidate the reasons since surface chemical properties of a catalyst-sorbent are reported to be important to SO_2 and NO removal activities, and a high basicity benefits SO_2 removal and a strong acidity benefits NO removal [14,15].

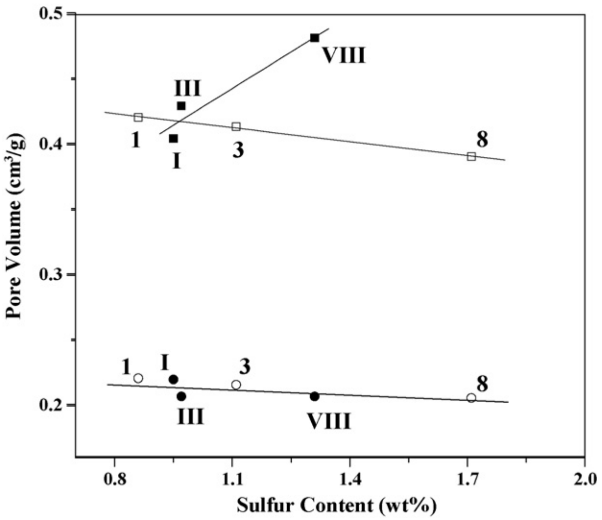

Fig. 7. Relations of sulfur content and total pore volume (square symbols)/ micro-pore volume (circle symbols) of V/AC samples. Arab and Roman numerals denote number of SO_2/NO removal-regeneration cycles with regeneration in 5% NH_3/Ar (open symbols) and Ar (filled symbols), respectively.

Nitrogen content is usually used to evaluate the AC's basicity [16] and the results of some of V/AC samples are shown in Table 2. Among all the samples listed, V/AC-F has the lowest N content, 0.45 wt%. After simultaneous SO_2 and NO removal at 200 °C, the N content increases to 0.78 wt% (V/AC-S), indicating that some of NH_3 added for SCR of NO is adsorbed on the V/AC during SO_2 and NO removal. The first Ar-regeneration reduces the N content to 0.61 wt% (Ar-300-1), but this value is still higher than that of V/AC-F. This indicates that some of the adsorbed NH_3 cannot be removed by the Ar-regeneration at 300 °C. The N content progressively increases with increasing SO_2/NO removal-regeneration cycle, 1.04 wt% for Ar-300-3 and 1.51 wt% for Ar-300-8, which further confirms adsorption of NH_3 on V/AC during the SO_2 and NO removal at 200 °C and that some of the adsorbed NH_3 is stable at the regeneration temperature of 300 °C.

The increase in N content is more significant for V/AC regenerated in 5% NH_3/Ar. After the first SO_2/NO removal-regeneration cycle, the V/AC (NH_3-300-1) shows an N content of 1.69 wt%, which is far higher than that of V/AC regenerated in Ar (Ar-300-1). After 8 SO_2/NO removal-regeneration cycles, the N content of NH_3-300-8 becomes even higher, 3.61 wt%. Compared N contents with the SO_2 capture capacities shown in Fig. 3, it can be found that the changes in N content cannot account for the difference in SO_2 capture capacity, since the highest SC_{80} is observed for samples with the lowest (V/AC-F) and the highest (NH_3-300-8) N contents.

Table 2 also presents the V/AC's acidity determined by NaOH titration. As expected, V/AC-F shows the lowest acidity, 1.13 mmol/g, and V/AC-S shows the highest acidity, 2.60 mmol/g. Consecutive SO_2/NO removal-regeneration increases the V/AC's acidity, regardless of the regeneration atmosphere. Regeneration in Ar results in higher acidities, 1.75 mmol/g or more, while regeneration in 5% NH_3/Ar results in relatively lower acidities, 1.56 mmol/g or less. Obviously, the presence of NH_3 during the regeneration, compared to the

Table 2
Surface acid properties and nitrogen contents of various V/AC

Samples	Acidic groups (mmol/g)	Nitrogen content (wt%)	SO_2 capacity (mg/g)
V/AC-F	1.13	0.45	60
V/AC-S	2.60	0.78	–
Ar-300-1	1.75	0.61	37
Ar-300-3	2.02	1.04	23
Ar-300-8	2.14	1.51	11
NH_3-300-1	1.34	1.69	60
NH_3-300-3	1.56	2.92	61
NH_3-300-5	1.51	–	57
NH_3-300-8	1.50	3.61	58
NH_3-300-1	1.34	1.69	60

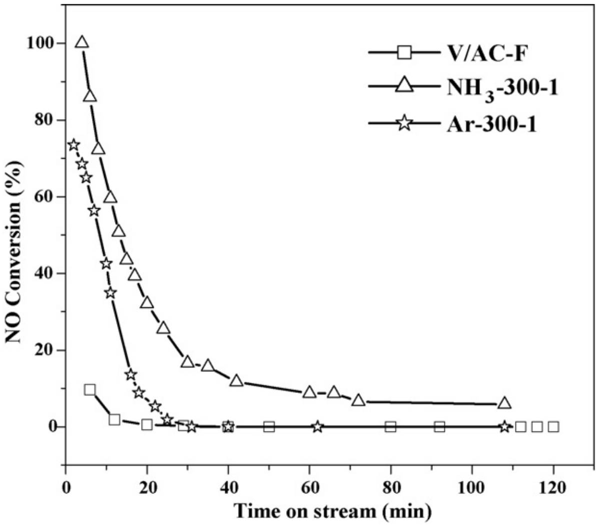

Fig. 8. NO conversion in the absence of gaseous NH_3 for various V/AC. Conditions: 200 °C, 600 ppm NO, 5% O_2 and balance Ar.

absence of NH_3, reduces the V/AC's acidity, even though 5% NH_3/Ar-regenerated samples have higher sulfur contents (see Table 1. sulfur is usually considered to present acidity). This possibly results from their higher N contents due to NH_3 adsorption during regeneration. If not for the NH_3 adsorption, the acidity of V/AC regenerated in 5% NH_3/Ar would be higher than that regenerated in Ar, as indicated by the sulfur content data in Table 1.

In general, it is believed that a higher surface acidity benefits SCR of NO due to increased NH_3 adsorption. The data presented so far indicate, however, that V/AC samples regenerated in 5% NH_3/Ar have lower acidities but higher NO conversions, compared to those regenerated in Ar. This discrepancy is exclusively due to the difference in N content since SCR of NO by AC-based catalyst-sorbents is reported to mainly involve the adsorbed NH_3 [17]. To elucidate the role of this N or NH_3 on SCR of NO, Fig. 8 compares NO conversions of various V/AC at 200 °C in the absence of gaseous NH_3. As can be seen, V/AC-F shows a low initial NO conversion, while Ar-300-1 shows a higher NO conversion in the early stage and NH_3-300-1 shows even higher NO conversion. These data indicate that N remained in Ar-300-1 and NH_3-300-1 may participate in the SCR reaction, which well explain the increased NO conversion of V/AC after regeneration (Figs. 1 and 2).

3.4. Regeneration mechanism

The data and discussions presented above show that:

1. SO_2 desorption is not affected by the presence of NH_3 and CO_2 evolves concurrently with SO_2 evolution although NH_3 reduces its amount. These indicate that "adsorbed SO_2" or H_2SO_4 are reduced mainly by carbon in V/AC. Since H_2SO_4 stores mainly in the micro-pores, its reduction by carbon is inevitable and the effect of regeneration atmosphere is limited by pore diffusion.
2. The presence of NH_3 reduces CO_2 evolution during SO_2 release but promotes releases of H_2O and H_2S. These indicate that NH_3 inhibits carbon consumption by substituting some of the carbon for H_2SO_4 reduction and substituting almost all the carbon for reaction with oxygen in V/AC.

Based on these generalizations, reactions involving in the regenerations can be written as:

- In Ar atmosphere:

$$C + 2H_2SO_4 = CO_2 + 2SO_2 + 2H_2O$$
(for a small amount of C)

$$C + 2O\,(\text{in V/AC}) = CO_2 \text{ (for a large amount of C and O)}$$

- In 5% NH_3/Ar atmosphere:

$$C + 2H_2SO_4 = CO_2 + 2SO_2 + 2H_2O$$
(for a small amount of C)

$$C + 2O\,(\text{in V/AC}) = CO_2 \text{ (for a very small amount of C)}$$

$$2NH_3 + 3H_2SO_4 = N_2 + 3SO_2 + 6H_2O$$
(for a small amount of H_2SO_4)

$$2NH_3 + 3O\,(\text{in V/AC}) = 3H_2O + N_2$$
(for a large amount of O)

4. Conclusions

(1) Supporting V_2O_5 on an activated coke results in a catalyst-sorbent (V/AC) active for simultaneous SO_2 and NO removal at 200 °C. The used V/AC can be regenerated in Ar at an optimum temperature of 380 °C or in 5% NH_3/Ar at an optimum temperature of 300 °C. The presence of NH_3 in regeneration results in higher SO_2 and NO removal activities than the absence of NH_3.

(2) Two types of reactions occur during the regeneration, reduction of the "adsorbed-SO_2" and reaction of carbon and oxygen in the V/AC. The former is accomplished mainly by oxidation of carbon in the V/AC. The latter is very significant in an Ar atmosphere and consumes more carbon than the former. The presence of NH_3 suppresses these two types of reactions especially the latter, and prevents widening of meso- and macro-pores in V/AC.

(3) Some of the NH_3 fed for SCR of NO at 200 °C forms N-containing species on V/AC, which is stable during regeneration at 300 °C. The presence of NH_3 in the regeneration results in more N-containing species to be formed on V/AC. These N-containing species promote SCR of NO in the subsequent SO_2/NO removal process.

Acknowledgement

The authors gratefully acknowledge the financial support from the Natural Science Foundation of China (20736001 and 20503038).

References

[1] G. Xie, Z. Liu, Z. Zhu, Q. Liu, J. Ge, Z. Huang, J. Catal. 224 (2004) 36.
[2] Q. Liu, C. Li, Y. Li, Carbon 41 (2003) 2217.
[3] J. Bimer, P.D. Sałbut, S. Berłożecki, J.P. Boudou, E. Broniek, T. Siemieniewska, Fuel 77 (1998) 519.
[4] P. Davini, Carbon 28 (1990) 565.
[5] B. Rubio, M.T. Izquierdo, A.M. Mastral, Carbon 36 (1998) 263.
[6] D.G. Olson, K. Tsuji, I. Shiraishi, Fuel Process. Technol. 65–66 (2000) 393.
[7] K. Knoblauch, E. Richter, H. Jüntgen, Fuel 60 (1981) 832.
[8] P. Davini, Fuel 68 (1989) 145.
[9] J. Ma, Z. Liu, S. Guo, J. Fuel Chem. Technol. (Chin.) 33 (2005) 6.
[10] Y. Wang, Z. Huang, Z. Liu, Q. Liu, Carbon 42 (2004) 445.
[11] J. Ma, Z. Huang, Z. Liu, S. Guo, Chin. J. Catal. 26 (2005) 463.
[12] A.A. Lizzio, J.A. DeBarr, Energy Fuel 11 (1997) 284.
[13] E. Raymundo-Piñero, D. Cazorla-Amorós, C. Salinas-Martines de Lecea, A. Linares-Solano, Carbon 38 (2000) 335.
[14] K. Tsuji, I. Shiraishi, Fuel 76 (1997) 555.
[15] M.A. Fraga, E. Jordão, M.J. Mendes, M.M.A. Freitas, J.L. Faria, J.L. Figueiredo, J. Catal. 209 (2002) 355.
[16] A. Bagreev, S. Bashkova, T.J. Bandosz, Langmuir 18 (2002) 1257.
[17] H. Teng, Y.-T. Tu, Y.-C. Lai, C.-C. Lin, Carbon 39 (2001) 575.