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Enhanced removal of hydrogen sulfide from a gas stream by 3-aminopropyltriethoxysilane-surface-functionalized activated carbon

Senlin Tian · Hong Mo · Renfeng Zhang · Ping Ning · Tinghua Zhou

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Abstract A commercial activated carbon was functionally modified by silylation with 3-aminopropyltriethoxysilane (APTES). The silylation led to the fixation of weakly basic functional groups, $-NH_2$, on the surface as indicated by pH titration, Boehm titration, N_2– BET analysis and X-ray photoelectron spectroscopic (XPS) analysis. Despite reducing the specific BET area and the pore volume, silylation improved the H_2S removal capacity so that APTES modified activated carbon (APTES-AC) was 3.55 times more effective than the original activated carbon. XPS results indicate that H_2S removal may be associated with the amino ($-NH_2$) group and the presence of sulfur in the four oxidation states S^{2-}, S^0, S^{4+} and S^{6+}. The effects of moisture, oxygen content and temperature on the performance of APTES-AC for H_2S removal were investigated. The presence of moisture in the gas stream was found to have an adverse effect on the H_2S removal, whilst the presence of oxygen favored the removal of H_2S by APTES-AC. The higher removal capacity of APTES-AC relative to the original activated carbon indicates that APTES-AC is a potential candidate for the removal of H_2S from gas streams. The H_2S removal efficiency of APTES-AC was proved be superior to that of Na_2CO_3-impregnated AC by the pilot-scale test of purification H_2S containing industrial waste gas, yellow phosphorus off-gas.

Keywords Activated carbon · Silylation · 3-Aminopropyltriethoxysilane · Hydrogen sulfide · Removal

1 Introduction

H_2S is a toxic, odorous and corrosive gas which is one of the more abundant pollutants of the atmosphere. The burning of H_2S releases SO_2, which is also a corrosive and toxic gas (Glass 1990). Major sources of H_2S include petroleum refineries, municipal waste water treatment plants, Kraft mills, viscose plants, coke ovens, coal gasifiers, anaerobic digestion of biosolids, animal processing plants, food-processing plants, semiconductor plants, and pharmaceutical plants, etc. (Masuda et al. 1999; Tsai et al. 2001; Feng et al. 2005; Hudson et al. 1974). Because of environmental, safety, and corrosion considerations, the removal of H_2S is necessary not only for pollution control but also for effective use of gas mixtures such as natural gas and biogas.

Many commercial processes are available for the removal of H_2S (Feng et al. 2005). Among the various methods for removal of H_2S, the Claus process, absorption/stripping and adsorption/oxidation are the most common and widely used (Glass 1990). Since typical tail gas from a Claus plant contains about 0.8% to 1.5% H_2S, Claus plants are still required to reduce H_2S emissions from the tail gas (Tsai et al. 2001). The gas-liquid absorption/stripping process using aqueous solutions of alkanolamines is one of the traditional treatment methods for removal of H_2S. In general, H_2S is thought to react almost instantaneously with the alkanolamines by proton transfer during this processes, as follows (Mandal and Bandyopadhyay 2005):

$$H_2S + RNH_2 \rightarrow RNH_3^+ + HS^- \quad (1)$$

S. Tian (✉) · H. Mo · R. Zhang · P. Ning · T. Zhou
Faculty of Environmental Science and Engineering, Kunming University of Science and Technology, Kunming 650093, P.R. China
e-mail: tiansenlin@sina.com

S. Tian
e-mail: tiansenlin@kmust.edu.cn

Despite being a mature technology that is applied extensively today, the gas-liquid absorption/stripping process requires highly energy-intensive regeneration of the solvents and is also plagued by corrosion problems (Huang and Yang 2003).

Adsorption/oxidation is one of the most reliable and highly efficient processes for removal of low concentrations of H_2S. Molecular sieves, silica gel and activated carbons, amongst others, have been used as adsorbents. Activated carbons have been proven to be effective adsorbents for the removal of H_2S. Compared with other adsorbents, the advantages of activated carbon are high surface area development, microporosity, thermal stability, high removal capacity of H_2S in moist air steams, and low costs per unit volume of adsorber. Moreover, activated carbon surface properties can be easily modified using various physical and chemical methods (Adib et al. 1999). During the adsorption/oxidation process using activated carbons, H_2S is not only adsorbed but is also oxidized due to the catalytic effect of the carbon surface. Besides the high surface area, the pore size distribution and surface chemical features both have a significant effect on the performance of materials used as H_2S adsorbents (Tsai et al. 2001; Feng et al. 2005; Chingombe et al. 2005; Bandosz 1999). The modification of surface chemistry has been found to be effective for improving removal capacity of H_2S on activated carbons (Feng et al. 2005). The most popular method of modification applied for activated carbons used in large quantities is its impregnation with various chemicals (Feng et al. 2005). Compared with virgin carbons, impregnated activated carbons in H_2S removal have higher efficiency and faster reaction kinetics (Yan et al. 2002). It was demonstrated that a basic surface environment favors the formation of elemental sulfur (sulfur radicals) and yields high removal capacities (Bandosz 1999). Therefore, activated carbons impregnated with alkaline materials such as NaOH and KOH, which promote an acid-base reaction at the carbon surface, are used for the removal of H_2S. The surfaces of activated carbons are usually impregnated with active species such as, for instance, potassium iodide, transition metals, or urea (Yan et al. 2002). The introduction of nitrogen-containing functional groups onto an activated carbon surface has also been achieved and has been reported to increase the adsorption capacity of H_2S (Chingombe et al. 2005). Nitrogen-enriched carbons can be obtained by chemical modifications of activated carbons, in reactions with various reagents that introduce the nitrogen groups (Bimer et al. 1998). There are several impregnation solutions that may increase the adsorption capacity of H_2S, such as methulol-melamine-urea, *n*-butylamine, and urea. However, these impregnated alkaline species were less stable and were released when the activated carbon was regenerated.

The strong affinity of alkanolamine groups for H_2S has been demonstrated and utilized in the gas-liquid absorption/stripping process. If amino groups are chemically grafted on to the surface, the modified nitrogen-enriched activated carbon is stabilized and high adsorption capacities of H_2S are obtained. On the other hand, the silylation of porous and nonporous solid materials has been widely used in different fields. The silylating agents make possible the covalent attachment of functional groups by displacement of active hydrogen atoms originally attached to hydroxyl groups by organosilyl derivatives of precursor silane (da Silva et al. 2007). The idea of grafting functional groups onto the surfaces of solid materials is a known strategy for the design of promising new adsorbents and catalysts. Previous studies have also confirmed that various adsorbents (silica xerogel and MCM-48) with covalently bonded amino groups have improved the efficiency of H_2S removal. A similar reaction is expected for activated carbon because it possesses acidic hydroxyl groups on its surface.

In recent years, the silylation technique has been applied to modify carbonaceous materials. This enables the control of the surface properties of the host carbons, and interesting results such as selective adsorption have been reported. Functional groups such as amino groups have been bonded to the surface of carbons using various chemical techniques. When amino groups were introduced onto the surface of activated carbons, enhanced or selective adsorption of nitrogen oxide and formaldehyde ions has been reported (Matsuo et al. 2007). Alkyl chains were successfully introduced onto the surface of graphite oxide layers by Si–O bonding using alkylchlorosilanes. By using silylating reagents containing amino groups such as 3-aminopropyltriethoxysilane, it would be possible to introduce amino groups onto the surface of activated carbon (Matsuo et al. 2007).

To our knowledge, the literature contains no reports on H_2S removal by organosilane with $-NH_2$ group surface-modified activated carbon. In this study, activated carbons were modified by silylation with a typical organosilane with an $-NH_2$ group, namely 3-aminopropyltriethoxysilane (abbreviated as APTES), in order to obtain modified activated carbons with different surface properties. The main aim of the present paper is to ascertain the feasibility of enhancing the selective H_2S removal efficiency of activated carbons. The removal efficiency of APTES silylated activated carbons was also compared with the corresponding fresh activated carbon and the other modified activated carbon. Physicochemical properties including surface area, average pore diameter, micropore volume and chemical structure of the activated carbons were characterized by N_2 adsorption/desorption experiments, X-ray photoelectron spectroscopy (XPS), Boehm titration, and determination of carbon surface pH. The influences of several main factors such as moisture, oxygen content and temperature on the efficiency of H_2S removal by activated carbon were also investigated.

2 Materials and methods

2.1 Materials

A coal-based commercial granular activated carbon, ZP-3, was obtained from the Shanxi Taiyuan Actived Carbon Factory, China, and used as a starting material in the present investigations. Before the modification processes, the activated carbon was washed with deionized water and dried at 120 °C for 24 h. APTES at 95% purity was used as received from the Shanghai Yaohua Chemical Plant. Analytic grade toluene and dichloromethane were purchased from Bodi Chemical Co., Ltd, China, and were used without further purification.

2.2 Preparation of adsorbents

9.0 g of the washed and dried activated carbon was placed into a three-necked flask. 150 ml of toluene and 45 ml of APTES were then added to the flask. The mixture was blended and stirred thoroughly. The flask was put into a rotary evaporator, refluxed at 70 °C for 5 h and then filtered. The solid product was distilled twice with 375 ml of dichloromethane for 10 h in a Saxhlet. The modified activated carbon was then air dried at 110 °C for 12 h. The original and modified activated carbons are referred to as AC and APTES-AC, respectively.

The Na_2CO_3-impregnated activated carbon (Na_2CO_3–AC) was prepared according to the following procedure. Approximate 20 g AC was washed three times with distilled water, then dipped into 100 ml of Na_2CO_3 aqueous solution (0.1 mol/L) for 24 h. Further, it was dried at a temperature of 110 °C for 15 h.

2.3 N_2 adsorption/desorption

The nitrogen adsorption-desorption isotherms were measured with an automatic adsorption instrument (Quantachrome Autosorb NOVA 2000e). Prior to measurement, the samples were outgassed at 150 °C for 10 h. The nitrogen adsorption-desorption data were recorded at -196 °C. Specific surface area was determined by the Multipoint Brunauer-Emmett-Teller (BET) method. The total pore volumes were estimated by the liquid volume of adsorbate (N_2) at a relative pressure of 0.98. The pore size distributions were determined by the Barrett, Joyner and Halenda (BJH) model to the desorption branch of the nitrogen adsorption-desorption isotherms.

2.4 X-ray photoelectron spectroscopy

XPS measurements were taken using a Physical Electronics (Model PHI5600 ESCA) spectrometer. The spectrophotometer was ASTM Calibrated and operated under vacuum (5×10^{-9} Torr). Non-monochromatic $K\alpha$ X-rays (200 W) at a take-off angle of 45° were used as the primary excitation source, with an analysis area 0.8 mm^2 on the sample surface. Survey seams in the range of 1–1100 eV were recorded at a pass energy of 185.85 eV and with a step size of 0.8 eV. The carbon C_{1s} electron binding energy (BE) corresponding to graphitic carbon was referenced at 284.8 eV for calibration purposes. The data were analyzed using a Gaussian–Lorentzian linear least squares fitting program.

2.5 pH of the activated carbon surface

The pH of the activated carbon surfaces before and after silylation was measured in the following way. 2.50 g of dry sample was added to 50 ml of hot fresh distilled water, boiled for 5 min, and cooled to room temperature. The suspension was stirred overnight to reach equilibrium. The sample was then filtered and the pH of the solution was measured.

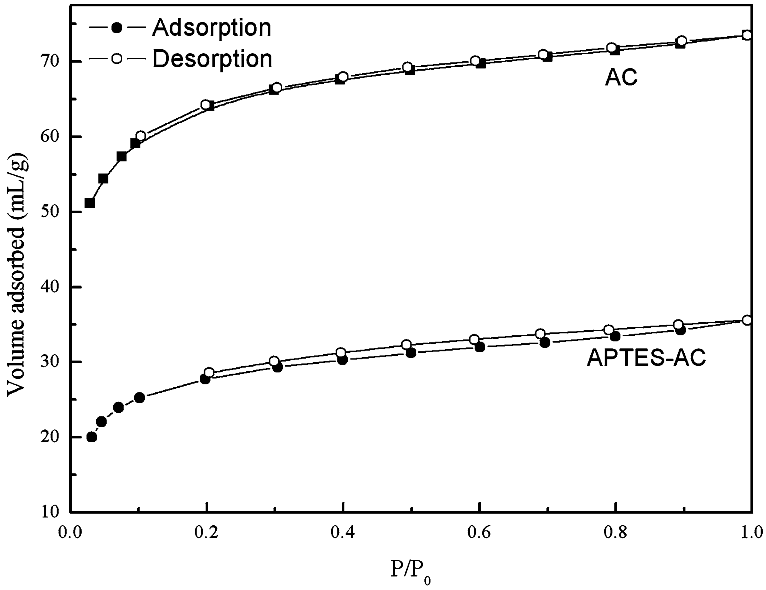
2.6 Boehm titration

The surface groups were determined according to the method of Boehm. 1.00 g of carbon sample was placed in 50 ml of the following 0.1 mol/L solutions: NaOH, Na_2CO_3, $NaHCO_3$, and HCl. The vials were sealed and shaken for 1 h, then taken out and placed at room temperature for 24 h. The suspension was filtered. 5 ml of each filtrate was pipetted and the excess of base or acid was titrated with 0.1 mol/L solutions of HCl or NaOH, respectively. The numbers of acidic sites of various types were calculated under the assumption that NaOH neutralizes carboxylic, phenolic, and lactonic groups; Na_2CO_3 neutralizes carboxylic and lactonic groups; and $NaHCO_3$ only neutralizes carboxylic groups. The number of surface basic sites was calculated from the amount of HCl which reacted with the carbon.

2.7 H_2S adsorption experiments

The H_2S removal capacity of various samples was evaluated by a dynamic test. The experimental procedures are as follows. The first gas flow was nitrogen, supplied from a gas cylinder (99.999% purity) and, where necessary, humidified by passage through water maintained at a pre-set temperature. The stream humidity in the gas flow was gravimetrically measured with anhydrous silica gel. The second gas flow was H_2S supplied from a gas cylinder. Oxygen supplied from a gas cylinder (99.999% purity) was passed through the third gas flow and then mixed with the above two gas flows in a gas mixer. The mixed gas was passed through the adsorption column. The temperature of the column was maintained and controlled by a water bath. The total gas flow rate was 90 ml/min. The concentration of hydrogen sulfide and

Fig. 1 Nitrogen adsorption-desorption isotherms of activated carbons before and after silylation at −196 °C



the content of oxygen were regulated by changing the flow rate of various gas flows and monitored by a Gas Chromatograph (GC-14C, Japan) by a flame photometry detector.

The adsorption column was 30 cm in length and 10 mm in diameter. The column was widened at the top to a diameter of 20 mm to minimize possible wall effect according to the experience from that reported (Bagreev and Bandosz 2005). The bottom of the adsorption column was packed with 10 cm of quartz wool to ensure the adsorbates were well mixed. The weighed adsorbent sample was packed into the adsorption column over the quartz wool. The concentration of H_2S was analyzed by a Gas Chromatograph (GC-14C, Japan) with a flame photometry detector. The "breakthrough time" is defined as the time at which the H_2S outlet concentration reaches 5% of the inlet concentration during the determination of breakthrough curves. According to the results of preliminary test, while outlet concentration of H_2S approximate to inlet concentration (e.g. $C/C_0 = 0.95$), the change of removal capacity is inappreciable. So the dynamic removal capacity of H_2S was measured until the ratio of C (outlet concentration)/C_o (inlet concentration) was 0.95. The isotherms of H_2S were carried out by a dynamic method. The adsorbed capacity of H_2S was obtained by integrating the area above the breakthrough curve. The adsorption isotherm curves of H_2S were plotted with the data of adsorbed capacity obtained at the various H_2S concentrations under certain conditions.

2.8 Demonstrated purification process

The challenge gas stream was off-gas produced in the process of yellow phosphorus at yellow phosphorus plant of Jianglin Group Co, Ltd., Yunnan, China. The demonstrated experiments were performed at Jianglin Group Co, Ltd. The challenge gas stream was metered at 140 ml/min through a cylindrical carbon bed (50 cm in length and 2 cm in diameter), corresponding to a space velocity of 800 h^{-}. The other testing conditions are as the following: the carbon bed temperature of 24 °C, adsorbent dose of 15 g, H_2S inlet concentration of 104 ppm, particle diameter of adsorbents of 0.5 mm, space velocity of 800 h^{-}, RH = 0, oxygen content of 0.5%. The breakthrough curves of the APTES-AC and Na_2CO_3−AC under the above-mentioned conditions were test and compared.

Table 1 Pore and surface characteristics of AC and APTES-AC

Sample	BET surface area (m^2/g)	Total pore volume (ml/g)	Average pore radius (Å)
AC	837.37	0.47	11.16
APTES-AC	304.39	0.18	12.17

3 Results and discussion

3.1 Effect of silylation on pore structure

Figure 1 shows the nitrogen adsorption-desorption isotherms of activated carbon before and after silylation, respectively. Pore distributions for AC and APTES-AC are shown in Fig. 2. The BET surface area, total pore volume and average pore radius are listed in Table 1. Shapes of the isotherms indicate some differences in porous structure between unsilylated and silylated activated carbons. According to the IUPAC classification, the isotherms of AC and APTES-AC are all of type I with a well-defined plateau and are characteristic of microporous materials. The isotherms are concave

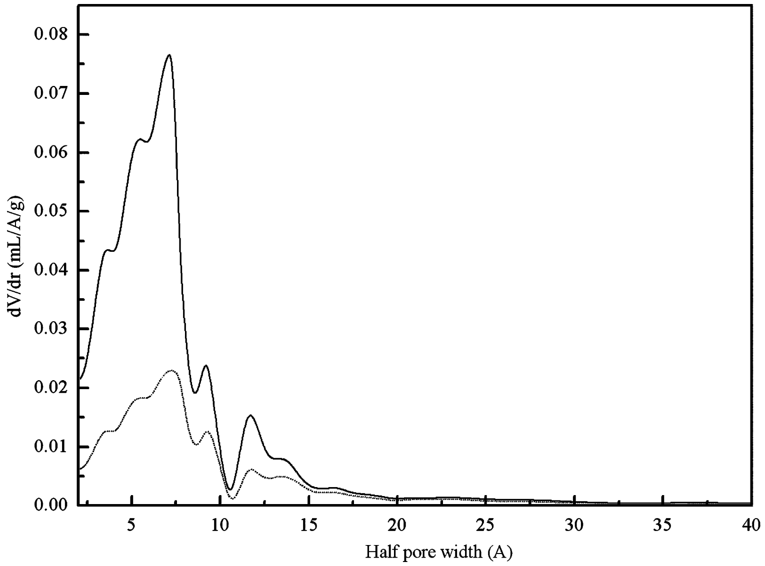


Fig. 2 Pore distributions for AC (*solid line*) and APTES-AC (*dotted line*)

to the P/P_0 axis and the adsorption capacity approaches a limiting value as P/P_0 approaches 1, indicating that the limiting adsorption capacities for activated carbons before and after silylation are all governed by the accessible micropore volume rather than by the internal surface area. The desorption hysteresis loops due to capillary condensation in mesopores are not very obvious for AC, indicating that the adsorbents possess only a few mesopores. However, the loop areas increase slightly from AC to APTES-AC, indicating that silylation develops more mesoporosity or reduces some microporosity. Upon silylation, significant decreases in the surface area and pore volume were observed. The BET area of AC decreased from 837.37 to 304.39 m^2/g in APTES-AC. A corresponding decrease in pore volume was also observed from 0.47 to 0.18 ml/g. The BET surface area and pore volume of the silylated activated carbon decreased by about 63.7% and 61.7% relative to the initial activated carbon. This is a result of pore blockage in the micropores caused by the groups grafted on during the silylation process, where the coating of the groups of organosilanes results in an increase in the size of the agglomerates or packed particles, leading to a decrease in the adsorption capacity of APTES-AC. Similar results have been reported that silylation with methyltrimethoxy silane (MTMS) reduced the specific areas of activated carbons by 25–40% (Graw et al. 1992). In addition, the pore size distribution as determined by applying the BJH model to the desorption branch of the nitrogen adsorption-desorption isotherms, also underwent slight changes during silylation. The pore size was slightly broadened due to the presence of the coating. The average pore radius of the silylated samples increased slightly with respect to the original carbon, from 11.16 to 12.17 Å. This is opposite to observations of the silylation of MCM-41 where the pore diameter decreased after silylation (Huang and Yang 2003). Figure 2 shows that, apart from a significant decrease in the pore volume, the curves of pore size distributions for both samples are similar.

Table 2 The pH of the carbon surface and the number of groups evaluated from Boehm titration (mmol/g)

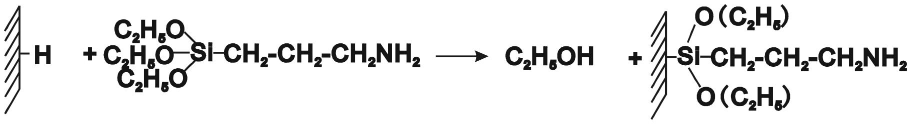
Sample	pH	Carboxylic	Lactonic	Phenolic	Acidic	Basic
AC	6.8	0.00	0.18	0.26	0.44	0.28
APTES-AC	9.1	0.01	0.08	0.19	0.28	0.51

3.2 pH and Boehm titration

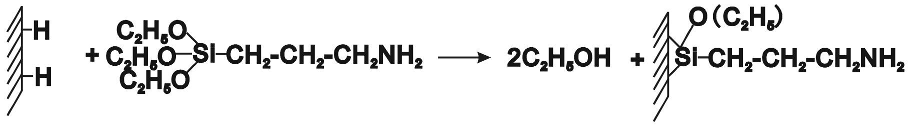
The average pH of the carbon surface was found to play an important role in the removal of hydrogen sulfide (Adib et al. 1999). The results of pH measurement are summarized in Table 2. It is noteworthy that the pH of activated carbon significantly increased, from 6.8 to 9.1, after modification with APTES. This implies that silylation with APTES provides the necessary increase in the surface pH of carbon, consequently improving the removal of H_2S (Yan et al. 2002). Boehm titration is most commonly used to determine the surface functional groups of activated carbon (Yan et al. 2002). Using this method, the amounts of carboxylic, lactonic and phenolic groups, and the number of basic surface sites, are obtained and presented in Table 2. Based on these results it is clearly seen that the two samples, from before and after silylation, differ in terms of their surface chemistry. The results for AC are in agreement with the pH measurements. The pH of AC is in the acidic range (6.8), whereas after silylation, the concentration of basic groups increases from 0.28 to 0.51 mmol/g while that of the acid groups decreases from 0.44 to 0.28 mmol/g. AC exhibits a weakly acidic surface characteristic because the acidic groups (0.44 mmol/g) are more abundant than the basic ones (0.28 mmol/g). APTES-AC is predominantly basic and has a much higher concentration of basic groups (0.51 mmol/g) than AC before silylation with APTES. On both AC and APTES-AC, the predominant acid groups are lactonic and phenolic groups. However, lactonic and phenolic group concentrations on APTES-AC are only 0.44 and 0.73 times those on AC, respectively. Analysis of these values indicates a significant increase in the basicity of APTES modified sample and highlights the important role of silylation for improving the amount of basic groups on activated carbon.

3.3 XPS

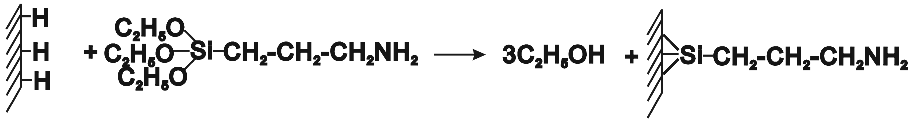
XPS has been shown to be a useful tool for analyzing the surface groups of activated carbons. It allows the semi-quantitative analysis of functional groups, by examining the shift in binding energies which depend on the local chemical environment (Jansen and van Bekkum 1995). XPS was employed to evaluate the surface chemical structure of AC, APTES-AC and H_2S-loaded APTES-AC in this study. In order to prepare a H_2S-loaded APTES-AC sample, 3.00 g of APTES-AC was subject to uptake of H_2S for 100 min at the following conditions: 30 °C, the inlet concentration of 1600 ppm, the gas flow of 90 ml/min, the particle diameter of 0.5 mm and the relative humidity (RH) of 0. Table 3 shows the major surface element concentrations of AC and APTES-AC obtained by XPS analysis. The concentrations of C and O on the AC are 93.56% and 6.44%, respectively. No Si could be detected on the AC. The concentrations of C, O and Si on the APTES-AC are 86.63%, 9.95% and 3.43%, respectively. Because the unreacted APTES was washed off in the distillation process with dichloromethane, the increase of Si content after silylation should be ascribed to the chemical fixation of alkylsilane groups onto the surface of AC and therefore confirms the occurrence of silylation reactions between APTES and the surface groups of activated carbon. Based on this result, the procedure we have followed to modify the surface of activated carbon is similar to that used extensively for silica and zeolite Y and proceeds by the possible reaction shown below (Singh and Dutta 1999):



(2)



(3)



(4)

Calculated from the data shown in Table 3, the mass ratio of O/C for APTES-AC is 0.11 and is larger than that for AC, which is 0.07. This means that the relative content of elemental oxygen increases after silylation. According to (2)–(4), three of the possible groups attached are:

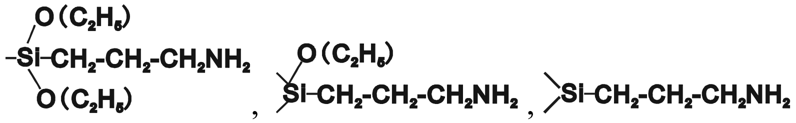


Table 3 Elemental analysis of AC and APTES-AC using XPS

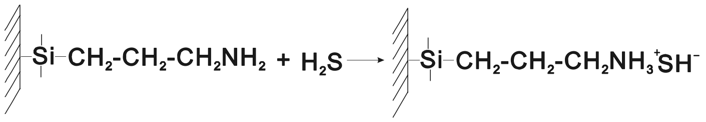
Sample	AC			APTES-AC		
	C_{1s}	O_{1s}	Si_{2p}	C_{1s}	O_{1s}	Si_{2p}
Area (cts-eV/s)	3748	658	0	3624	1061	159
Sensitivity factor	2.019	5.148	2.237	2.019	5.148	2.237
Concentration (%)	93.56	6.44	0.00	86.63	9.95	3.43

The mass ratios of O/C for these three groups are 0.38, 0.32 and 0.00, respectively. Since (4) cannot provide additional oxygen, the predominant reactions should be (2) and (3). That is to say, each APTES molecule will react with one or two reactive groups such as –OH.

Table 4 shows the binding energy of the C_{1s}, N_{1s}, O_{1s}, S_{2p} and Si_{2p} electrons. These distinct energies allow the identification of different species. According to the literature (Brazhnyk et al. 2007), the C_{1s} spectra were well fitted with five peaks (Table 4) assigned to carbon atoms bound with carbon and/or hydrogen atoms (BE = 284.76–284.80 eV), to carbon atoms bonded with oxygen atoms by one, two and three bonds (BE = 286.16–286.36, 287.57–287.67 and 289.04–289.09 eV, respectively) and to the π-π^* peak (BE = 290.99–291.15 eV). The data in Table 4 indicate that the silylation of activated carbon had little influence on the electronic state of carbon atoms and C_{1s}. However, the relative contents of contributory peaks vary after silylation. The silylation increased the intensity of peaks assigned to carbon-carbon and/or carbon-hydrogen from 66.46% to 75.01%. Furthermore, the relative intensities of the peaks assigned to carbon-oxygen groups and π-π^* peaks were decreased after silylation. These observations correspond to the results obtained by Boehm titration (Table 3), which showed a decrease in the amount of acid groups (lactonic and phenolic groups) after silylation. The results may be attributed to the induction of carbon-carbon and carbon-hydrogen containing groups of $-Si(CH_3CH_2O)_2CH_2CH_2CH_2NH_2$ and $-{=}Si(CH_3CH_2O)CH_2CH_2CH_2NH_2$ by the silylation reaction.

The O_{1s} spectra were fitted with three peaks and their binding energies, chemical shifts (Δ) and relative contents are also reported in Table 4. The O_{1s} peaks with BE = 530.4–531.0 eV were assigned to C=O type oxygen (C=O, COOR). The second O_{1s} peaks (BE = 533.2–533.8 eV) correspond to C–O type oxygen in C–OH and COOR groups. According to published data (Brazhnyk et al. 2007), the O_{1s} peaks with BE = 534.10–535.48 eV are associated with strongly adsorbed water molecules. The relative content of different oxygen species shows that silylation of activated carbon reduces the relative content of O_{1s} peaks corresponding to C–O type oxygen in C–OH and COOR groups from 72.55% to 34.13%. This corresponds to the reduction of the content of phenolic and lactonic groups as indicated by Boehm titration.

As shown in Table 4, nitrogen could not be detected in the AC sample by XPS analysis. In the XPS analysis of N_{1s} in APTES-AC, only one peak assigned to nitrogen was detected at 400.00 eV. This peak is usually associated with alkylamine groups (Jansen and van Bekkum 1995). Besides the peak corresponding to alkylamine groups, another peak assigned to nitrogen was determined at 402.28 eV for H_2S-loaded APTES-AC, which is associated with protonated amide (Jansen and van Bekkum 1995; Mangun et al. 2001). The occurrence of the N_{1s} peak at 402.28 eV shows that the removal of H_2S on APTES-AC is associated with alkylamine groups introduced by silylation. Huang and Yang (2003) have proved the formation of a $NH_3^+HS^-$ group from the weak chemical reaction between H_2S and surface amine groups ($-NH_2$) in the 3-aminopropyl functional silica xerogel and MCM-48. Therefore H_2S is thought to react with the alkylamine groups by proton transfer, which is similar to the reaction taking place during the aqueous absorption processes with amine. Accordingly, we assume the reaction between the amine groups ($-NH_2$) fixed on AC and H_2S may proceed as shown in (5):



$$\text{Si}-CH_2\text{-}CH_2\text{-}CH_2NH_2 + H_2S \longrightarrow \text{Si}-CH_2\text{-}CH_2\text{-}CH_2NH_3^+SH^- \qquad (5)$$

XPS analysis for S_{2p} was also conducted on H_2S-loaded APTES-AC to identify the reaction product. The binding energies and the relative contents for various sulfur species are shown in Table 4. Four peaks are observed at 164.38, 165.86, 168.71 and 170.07 eV, respectively. According to previous studies (Wang et al. 2001), these peaks can be at-

Table 4 Results of XPS analysis for C_{1s}, O_{1s}, N_{1s}, and S_{2p} of AC, APTES-AC and H_2S loaded APTES-AC[a]

Element	AC			APTES-AC			H_2S loaded APTES-AC[b]		
	Binding energy (eV)	Chemical shift (eV)	Relative content (%)	Binding energy (eV)	Chemical shift (eV)	Relative content (%)	Binding energy (eV)	Chemical shift (eV)	Relative content (%)
C_{1s}	284.76	0.00	66.46	284.80	0.00	75.01			
	286.16	1.40	16.17	286.36	1.55	12.08			
	287.57	2.81	6.39	287.67	2.87	5.97			
	289.04	4.28	6.34	289.09	4.29	4.12			
	291.15	6.39	4.63	290.99	6.18	2.82			
O_{1s}	531.24	0.00	13.42	532.00	0.00	39.09			
	532.55	1.31	72.55	533.46	1.46	34.13			
	534.10	2.86	14.03	535.48	3.48	26.78			
N_{1s}	N.D.			400.18	0.00	100.00	400.00	0.00	69.03
	N.D.			N.D.			402.28	2.28	30.97
S_{2p}	N.D.			N.D.			164.38	0.00	47.35
	N.D.			N.D.			165.86	1.48	15.55
	N.D.			N.D.			168.71	4.33	30.04
	N.D.			N.D.			170.07	5.68	7.07

[a] N.D means that "cannot be determined"

[b] XPS C_{1s} and O_{1s} of H_2S loaded APTES-AC sample have not been determined

tributed to the bonding energy of S^{2-}, S^0, S^{4+} and S^{6+}, respectively. As the results show in Table 4, the relative contents of the various S species are 47.35%, 15.55%, 30.04% and 7.07% for S^{2-}, S^0, S^{4+} and S^{6+}, respectively. This indicates that most of the H_2S molecules were not oxidized during the removal process and the main oxidation products are S^{4+} (30.04%), S^0 (15.55%) and S^{6+} (7.07%). Three principle phenomena are crucial, and they jointly influence the overall performance of the studied carbons: physical adsorption, chemisorption, and H_2S oxidation (Yan et al. 2002). These results also imply that both reaction with $-NH_2$ and catalytic oxidation are the predominant removal mechanisms of H_2S on APTES-AC.

3.4 Adsorption isotherms and removal capacity evaluation for silylated activated carbon

To provide evidence for the affinity of the new sites created for H_2S, AC and APTES-AC were measured and compared in a dynamic removal capacity test of H_2S. The breakthrough curves of H_2S on AC and APTES-AC are plotted in Fig. 3. The two breakthrough curves differ in their performance as H_2S adsorbents and clearly illustrate the efficiency of the treatment for H_2S removal. With APTES silylation, a significant improvement in H_2S removal is found, with a saturated removal time increasing from 240 min for AC to 840 min for APTES-AC. From the collected data the dynamic removal capacities of each sample were calculated by integration of the area above the breakthrough curves and from the concentration of H_2S in the inlet gas, flow rate, time, and mass of adsorbent. Comparing the two adsorbents, APTES-AC adsorbed more H_2S than AC: the H_2S removal capacity for APTES-AC (16.84 mg/g) is 3.55 times that for AC (4.74 mg/g).

In order to investigate the removal capacities of APTES-AC for the various concentration of H_2S and to understand the adsorption behavior of H_2S on APTES-AC, H_2S adsorption isotherm at 30 °C for APTES-AC was obtained by varying the H_2S concentration (250–8200 ppm). To enhance the removal capacity of activated carbon to H_2S, various methods have been used. The most common is impregnation of activated carbon with sodium or potassium hydroxide or salts containing potassium, such as sodium carbonate. Because of the acid characteristic of H_2S, impregnation with alkaline materials, which promote an acid-base reaction at the carbon surface, is the most common method used to modifying activated carbon for the removal of H_2S. Especially in previous studies, a sodium carbonate-impregnated activated carbon (Na_2CO_3–AC, origin carbon is same as that used in this study) has been proved to be an effective

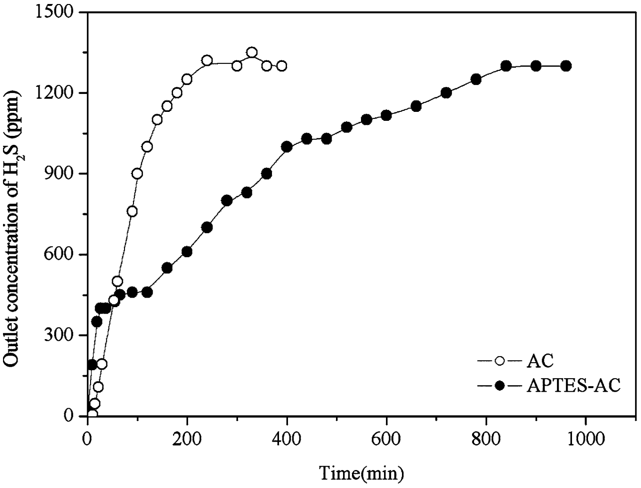


Fig. 3 Breakthrough curves of H_2S on AC and APTES-AC (30 °C, adsorbent dose of 3.37 g, inlet concentration of 1600 ppm, flow rate of 90 ml/min, particle diameter of 0.5 mm, RH = 0, oxygen content of 5%)

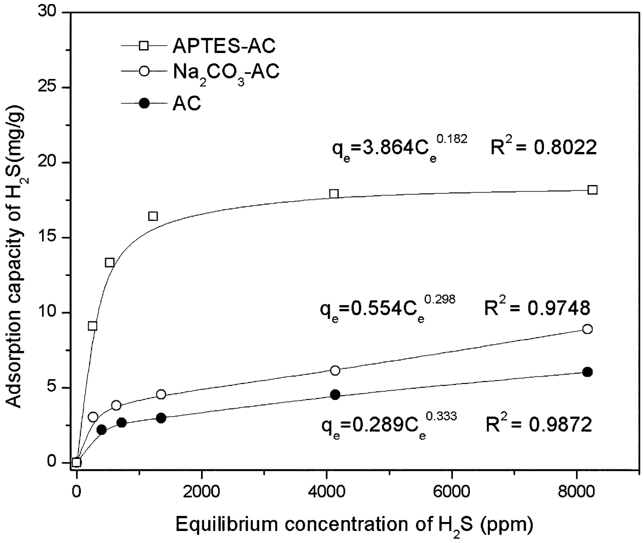


Fig. 4 Adsorption isotherm of H_2S on APTES-AC, Na_2CO_3–AC and AC (30 °C, particle diameter of 0.5 mm, RH = 0, oxygen content of 5%)

adsorbent for the removal of H_2S from a H_2S-containing industrial off-gas (Ning et al. 2005). So differences of adsorption properties among APTES-modified ACs and common alkaline-impregnated ones would be incarnated by the comparison of isotherms of APTES-AC, and Na_2CO_3–AC. The isotherms of APTES-AC, Na_2CO_3–AC and AC are shown in Fig. 4. The H_2S adsorption capacities considerably increased with the equilibrium concentration increasing from 250 to 8200 ppm for the three adsorbents. The isotherms show that APTES silylation can remarkably improve the H_2S removal by activated carbon. At the maximum equilibrium concentration tested (8200 ppm) the adsorption capacity is 18.13, 8.88 and 6.03 mg/g for APTES-AC, Na_2CO_3–AC and AC, respectively. The adsorption capacity of APTES-AC is approximately 2 and 3 times the values of Na_2CO_3–AC and AC, respectively.

The isotherm data from Fig. 4 were fitted to the Freundlich equation described below in (6):

$$q_e = K_f C_e^{1/n} \tag{6}$$

where q_e is the adsorption capacity (mg/g); C_e is the equilibrium concentration of H_2S in gas phase (ppm). The estimated parameters with the correlation coefficient (R^2) are also shown in Fig. 4. The correlation coefficients, R^2, show that the H_2S isotherms of the three adsorbents can be satisfactorily described by the Freundlich equation. In the Freundlich equation, K_f and $1/n$ are the constants related to adsorption capacity and intensity of adsorption, respectively. K_f values for APTES-AC (3.864) are larger than those for Na_2CO_3–AC and AC (0.554 and 0.289, respectively). According as K_f values, APTES-AC has a larger adsorption capacity than Na_2CO_3–AC and AC. $1/n$ values for between 0 and 1 represent good adsorption of H_2S on adsorbents. $1/n$ values also imply that the interaction between the APTES-AC and H_2S is greater than that between the Na_2CO_3–AC, AC and H_2S.

The above-mentioned results indicate that the silylation process results in a remarkable decrease in the nitrogen adsorption capacity reflected in a decrease in the specific area of APTES-AC. However, the surface area and pore volume are not the crucial factors that determine the final performance of carbons as hydrogen sulfide removers (Bandosz 2002). As indicated by the previous studies, surface basic groups represent possible active sites that are responsible for H_2S removal through acid/base interactions (Feng et al. 2005). The fact that hydrogen sulfide is an acidic gas also suggests that the presence of a basic environment plays a significant role in its removal. Therefore, since APTES-AC shows a higher removal capacity than AC for H_2S removal, APTES-AC is superior to AC for removal of H_2S.

3.5 Influence of moisture, oxygen content and temperature on removal of H_2S

Because a certain amount of water vapor is generally present in waste gas, the effect of moisture on the removal capabilities of H_2S plays an important role in the application of activated carbon for pollution control. The influence of stream humidity on the adsorption of H_2S on APTES-AC was also investigated and was quantified by analyzing the impact of moisture on the breakthrough time. Figure 5 shows the breakthrough curves of 1600 ppm H_2S removal by APTES-AC under gas streams with different RH. As shown in Fig. 5, the presence of moisture in the gas stream significantly decreases the H_2S removal capability of APTES-AC. Under dry conditions, the breakthrough

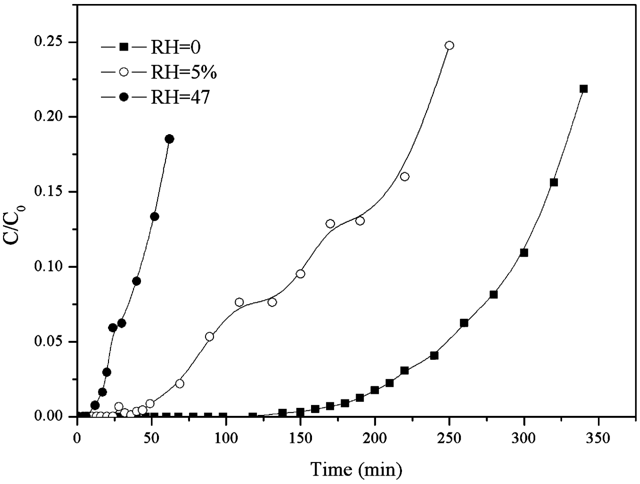


Fig. 5 Influence of moisture on the removal of H_2S with APTES-AC (30 °C, adsorbent dose of 3.37 g, inlet concentration of 1600 ppm, flow rate of 90 ml/min, particle diameter 0.5 mm, oxygen content of 4%)

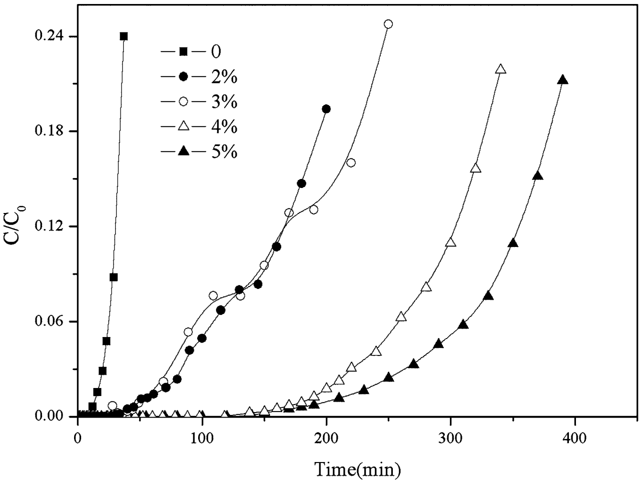


Fig. 6 Influence of oxygen content on the removal of H_2S on APTES-AC (30 °C, adsorbent dose of 3.37 g, inlet concentration of 1600 ppm, flow rate of 90 ml/min, particle diameter 0.5 mm, RH = 0)

time of APTES-AC is 246 min which is much longer than times obtained in moist conditions, which were 88 min and 24 min at RH = 5% and 47%, respectively. The effect of moisture on the adsorption/oxidation of H_2S is still disputed. The argument arises from the mechanisms involved. Water was found to have an adverse effect by blocking the active sites (Ghosh and Tollefson 1986). Nevertheless, based on a liquid film model, water was found to enhance the reaction by dissolving H_2S in water absorbed on the surface of activated carbon (Bagreev and Bandosz 2005). Some previous reports proposed that the H_2S dissolved and dissociated to produce H^+ and HS^- ions in the water film. Therefore, the absorption of H_2S into the water film increased the adsorption capability (Adib et al. 1999; Huang et al. 2006). However, unlike the effect that water has on H_2S removal on the common activated carbon in previous investigations, in this study water vapor did not improve the H_2S removal. This may be explained by both the physicosorption and chemisorption view points. Competition between H_2S and water for adsorption onto APTES-AC might occur when moisture exists in the gas stream, and in this case water vapor was difficult to condense as a water film onto the adsorbent during the adsorption process. Consequently, both water vapor and H_2S co-exist in the gaseous phase so that adsorption of water onto APTES-AC reduces the adsorption capacity for H_2S. Certainly, in order to confirm the adverse effect of water on adsorption of H_2S on APTES-AC, water vapor isotherm of APTES-AC need to be determined and compared with that of AC.

It has been proved that at least one of the removal approaches of H_2S was catalytic oxidation involving oxygen. The removal of H_2S by APTES-AC was investigated in the presence of various oxygen concentrations (Fig. 5). Significant differences were observed in the breakthrough times as the oxygen content was varied. The removal of H_2S was found to increase as the oxygen concentration increased. As indicated in Fig. 5, the breakthrough times were 87, 100, 244 and 298 min for oxygen concentrations of 2%, 3%, 4% and 5%, respectively, which are much longer that those obtained in the absence of oxygen (22 min). Obviously, the presence of oxygen can improve the H_2S removal significantly. One reasonable explanation is that oxygen in the gas stream would promote the catalytic oxidation process and favors the formation of elemental sulfur and partial conversion into sulfuric acid. The results also confirm that H_2S is removed by both adsorption and catalytic oxidation over APTES-AC, and that catalytic oxidation accounts for a considerable proportion of the removal capacities of H_2S.

Besides the moisture and oxygen content, temperature is also a principal influencing factor. The effect of temperature was studied by determination of the breakthrough curves of H_2S on APTES-AC at 20, 30 and 95 °C (Fig. 7). The removal of H_2S decreased gradually as the temperature increased from 20 to 95 °C. Increase of the slope at the turning point of the breakthrough curves with an increase of temperature indicated an increase in removal rate. However, an acceleration of breakthrough was observed with an increase of temperature from 20 to 95 °C. As mentioned above, mechanisms such as physical adsorption, chemical adsorption and catalytic oxidation all interact during the removal process of H_2S on APTES-AC. The temperature would exert an influence on all of the reactions of H_2S involving the above mechanisms. Higher temperatures will enhance catalytic oxidation and chemisorption but definitively suppress physical adsorption. Possibly, the reaction temperature in this study was insufficiently high to significantly enhance the catalytic oxidation of H_2S. With increased temperature, the physical adsorption capacity of carbon is believed to generally de-

Table 5 The contents of main ingredients of the challenge gas, yellow phosphorus off-gas

Ingredients	CO	CO_2	H_2	N_2	CH_4	H_2S	CS_2	COS	PH_3
Contents	90 vol%	2.5 vol%	4.5 vol%	3.5 vol%	0.3 vol%	104 ppm	76 ppm	77 ppm	945 ppm

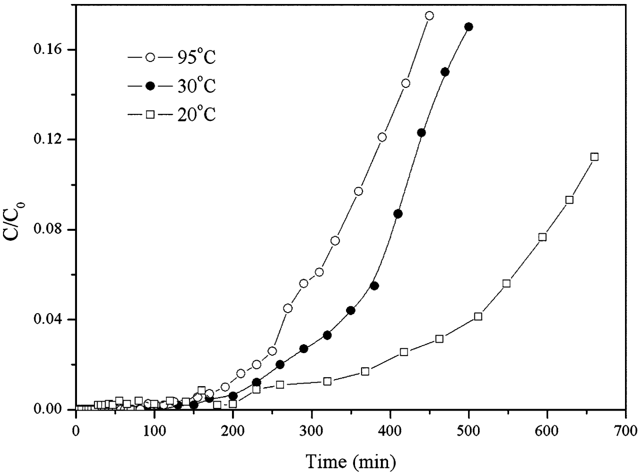


Fig. 7 Influence of temperature on the removal of H_2S (adsorbent dose of 3.37 g, inlet concentration of 1600 ppm, flow rate of 90 ml/min, particle diameter 0.5 mm, RH = 0, oxygen content of 3%)

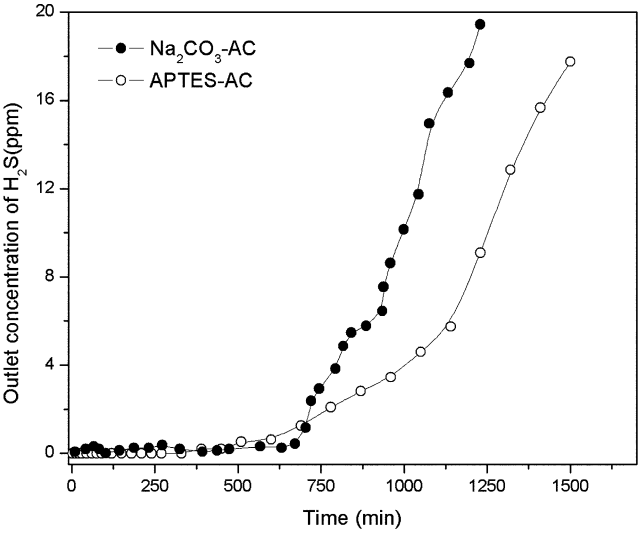


Fig. 8 Breakthrough curves for demonstrated purification of H_2S contained in yellow phosphorus off-gas (24 °C, adsorbent dose of 15 g, H_2S inlet concentration of 104 ppm, flow rate of 140 ml/min, particle diameter 0.5 mm, space velocity of 800 h^{-}, RH = 0, oxygen content of 0.5%)

crease, but the effect on chemisorption and catalytic oxidation is not so remarkable. The overall influence of elevating reaction temperature on H_2S removal is negative. Similar results for H_2S removal by alkaline activated carbons have been reported by Yan et al. (2004). These results also imply that APTES-AC is more suitable for serving as a H_2S adsorbent at lower temperatures.

3.6 Demonstrated purification application for yellow phosphorus off-gas

During the process of yellow phosphorus production, a great deal of off-gas, namely yellow phosphorus off-gas, would be emitted. For the purpose of utilization of CO contained in the off-gas (85–95 vol%), the impurities such as H_2S must be removed. Adsorption by modified activated carbon, especially by Na_2CO_3-impregnated activated carbon, has been proved to be one of effective methods for the removal of H_2S (Ning et al. 2005). A yellow phosphorus off-gas was used as challenge gas stream to test and compare the removal efficiencies of APTES-, Na_2CO_3–AC. The main ingredients of the off-gas are shown in Table 5. As the testing results depicted in Fig. 8, the breakthrough time (H_2S outlet concentration reaches 5% of the inlet concentration) of APTES-AC is 1100 min, which is longer than that of Na_2CO_3–AC (830 min). These results are generally consistent with those observed in laboratory-scale experiments. That is to say, APTES-AC can stand the test for the real waste gas. The results also indicate that compared with the common modified activated carbon, APTES-AC shows outstanding H_2S removal efficiency even under the conditions of real waste gas.

4 Conclusions

This study demonstrates the possibility to chemically modify the surface of activated carbon by APTES silylation. APTES-silylation of activated carbon decreases the specific surface area and pore volume, while the silylation favors the formation of surface basic groups. pH and Boehm titration results indicate a significant increase in the basicity of APTES modified sample and highlights the important role of silylation for improving the amount of basic groups on activated carbon. The introduction of weakly basic functional groups, $-NH_2$, can improve affinity of H_2S in AC. Thus the removal capacity of H_2S was enhanced after silylation. APTES-silylation can partly overcome the disadvantages for the traditional modification methods such as the instability and the releasing of impregnated alkaline species during the regeneration process. The adsorbed sulfur on APTES-AC was proved to be presented in the states of S^{2-}, S^0, S^{4+} and S^{6+} by XPS analysis. As the experimental results suggest, moisture, oxygen content and temperature play important roles in the removal of H_2S by APTES-AC. The presence of moisture in the gas stream and the elevation of reaction temperature were found to have adverse effects on the H_2S removal, whilst the presence of oxygen favored the removal of H_2S by APTES-AC. In summary, APTES-modified activated carbon can be employed as an efficient adsorbent for the removal of H_2S from a gas stream.

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