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Physicochemical properties and desulfurization activities of metal oxide/biomass-based activated carbons prepared by blending method

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Abstract Column activated carbons were prepared from walnut shell chars and transition metal oxide powders (i.e. Co_2O_3, Ni_2O_3, CuO and V_2O_5) with blending method. Samples were characterized by N_2 adsorption–desorption, X-ray diffraction, X-ray photoelectron spectroscopy and Fourier-transform infrared spectroscopy. The texture properties of all modified activated carbons with metal oxides dosage of <5 wt% did not change evidently. The basic functionalities of these activated carbons increased relative to blank carbon. Moreover, metal species with different oxidation states coexisted on the modified activated carbons. The optimal dosage of all metal oxides was 2 wt%. The sulfur capacities of these modified activated carbons were 7.7–46.0 % higher than that of blank activated carbon and the highest occurred for V_2O_5 modified activated carbon. The improved desulfurization performance was mainly attributed to the higher catalytic activity of the active metal oxides formed in the presence of O_2 during the desulfurization process.

Keywords Walnut shell · Activated carbon · Transition metals · Blending method · Desulfurization activity

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1 Introduction

Activated carbon is a carbonaceous adsorbent with high porosity, large surface area, variable surface chemistry characteristics and high surface reactivity. Activated carbon is widely used for environmental pollution control and in industrial processes as both adsorbent and catalyst. Among these applications, activated carbon based dry flue gas desulfurization methods attract worldwide attention due to their distinct advantages, such as their relatively simple procedures and higher SO_2 removal relative to wet scrubbing (Guo and Lua 2002). However, a large amount of activated carbon must be used in this process because the SO_2 capacity of normal activated carbon is low and can only be applied at low space velocity. Thus, this application can be very expensive. Therefore, it is important to develop a novel activated carbon from inexpensive raw materials with improved desulfurization activity.

Some agriculture byproducts are both inexpensive and abundantly available. In China, more than 1,00,000 tons of walnut shells are produced yearly (Yang and Qiu 2010). The reutilization of such wastes is useful for waste disposal and for exploiting their economic value. Walnut shells have high carbon content and low ash content, which makes them a good precursor for activated carbon production. Currently, it has been successfully applied for wastewater treatment (for example, the adsorption of dyes, heavy metal ions, etc.) (Kazemipour et al. 2008; Yang and Qiu 2010; Zabihi 2010). Nevertheless, little research has been conducted regarding the use of activated carbon derived from walnut shells for the removal of SO_2 from flue gas.

In addition, previous studies have found that the desulfurization activities of activated carbon could be improved by modification with transition metals, such as Co, Ni, Cu

and V (Gao et al. 2011; Guo et al. 2012; Tseng et al. 2003). Several procedures can be used practically to prepare activated carbon support catalysts. These procedures involve impregnation and blending methods. Impregnation methods generally include the addition of additives on as-received activated carbon, and followed by loaded activated carbon be calcined at 400–800 °C. In contrast, the blending method is performed by blending the carbon chars with additives before activation at 800–900 °C. This method is relatively simple and is referred to as one-step activation. Another difference between these two loading methods is the use of additive forms. Both solids and solutions can be used as additives for modifying activated carbon by blending method, but only solutions can be used when impregnation method is applied. Impregnation method has been widely used and studied (Afrane and Achaw 2008; Fan et al. 2012), however, very few studies regarding blending method have been published (Przepiórski 2005). The metal oxide is only distributed on the surface of activated carbon following impregnation method. In contrast, blending method results in the uniform distribution of additives throughout the carbon matrix (Przepiórski et al. 1999). In this study, the unique characteristics of blending method and the high temperature (900 °C in this study) used for metal oxides/carbon char activation are hypothesized to affect the physicochemical properties of the modified activated carbon, including the texture properties, functional groups and metal speciation. These properties are important factors that govern the sulfur capacity of activated carbon.

Therefore, the objective of this work was to investigate the effects of metal oxide blending on the physicochemical properties and SO_2 removal performance of activated carbon. First, transition metal oxides powders (Co_2O_3, Ni_2O_3, CuO and V_2O_5) were blended with walnut shell carbon chars. Next, the activated carbon was produced with one-step activation. The characterization and desulfurization activities of modified activated carbon were examined. Moreover, the possible desulfurization mechanisms of this novel catalyst were deduced.

2 Materials and methods

2.1 Preparation of activated carbon

Walnut shells used as the raw material for activated carbon preparation were obtained from Sichuan province, P. R. China. Elemental analysis showed that the walnut shells mainly consisted of (wt %): C 48.99 %, H 5.74 %, O 45.03 %, and N 0.24 %.

The walnut shells were crushed and sieved to obtain a final particle size of 0.14–0.28 mm. Next, the particles were carbonized in an electric furnace (SX2-8-10P, Chengdu, China) at 600 °C for 1 h at a constant heating rate of 5 °C/min. Subsequently, the chars were ground and passed through a 200-mesh screen before mixing with fine metal oxide powders (Co_2O_3, Ni_2O_3, CuO and V_2O_5, respectively) at weight ratios of 2, 5, 7 and 10 %, respectively. Afterwards, the mixtures were combined with hot coal tar (at approximately 60 °C), which served as the major binder, and carboxyl methyl cellulose (CMC) and/or polyvinyl butyral resin (PVB), which served as accessorial binders, These mixtures were stirred thoroughly in a 70 °C water bath before molding in a vacuum extruder a 3 mm diameter column. After formation, the molded carbon columns were activated at a temperature of 900 °C with a CO_2 flow of 1,000 mL/min for 2 h.

The prepared column activated carbons were named AC, AC-Co, AC-Ni, AC-Cu and AC-V based on the metal oxides that were used for modification. A weight percentage attached refers to the metal oxide dosage.

2.2 Activated carbon characterization

The BET surface area, pore volume and pore size distribution were calculated by nitrogen adsorption–desorption isotherms, obtained with an AUTOSORP ZXF-6 vacuum volumetric sorption instrument. X-ray diffraction (XRD) patterns were obtained with an X' PertPro MPD diffractometer at 30 kV and 20 mA employing Cu Kα radiation and step-scanning over 2θ range 10–80°. X-ray photoelectron spectra (XPS) analysis was applied to determine the surface chemical composition and functional groups with an ESCALAB 250XI spectrometer (Thermo Scientific, USA) using Al Kα radiation (1486.6 eV). XPS analysis was performed before and after the samples were etched using a 3 kV Ar^+ ion beam for 5 min. For Fourier-transform infrared spectroscopy (FTIR) characterization, a fixed weight of each sample was mixed with KBr before analysis. Transmission measurements were carried out in the 4,000–400 cm^{-1} region with a spectrometer (FTIR 670 NEXUS Nicolet, USA) at a resolution of 4 cm^{-1}. The content of surfaces site with acidic and basic characteristics were determined by the adsorption of benzoic acid (BA) and diphenylguanidine (DPG), respectively (Davini 1989).

2.3 Desulfurization experiment

The desulfurization experiments were carried out in a fixed-bed reactor system. A synthetic flue gas that contained 5,000 mg/m^3 SO_2, 9 vol% O_2, 10 vol% water vapor and was balanced by N_2 was preheated to 80 °C and passed through the columnar reactor (18 × 300 mm). This column contained 15 g of activated carbon at a space velocity of 600 h^{-1}. The SO_2 concentration was determined by

Table 1 Texture properties of activated carbons

Activated carbon	BET (m^2/g)	V total (cm^3/g)	Average pore radius (nm)
AC	565	0.380	1.565
AC-Co2	515	0.349	1.360
AC-Co5	641	0.420	1.855
AC-Co10	411	0.320	1.560
AC-Ni2	533	0.330	1.611
AC-Ni5	216	0.143	1.320
AC-Ni10	379	0.247	1.310
AC-Cu2	520	0.310	1.702
AC-Cu5	458	0.290	1.270
AC-Cu10	420	0.262	1.250
AC-V2	589	0.360	1.678
AC-V5	373	0.222	1.190
AC-V10	259	0.162	1.250

measuring the H_2SO_4 concentration with a NaOH solution after passing the gaseous mixture through a H_2O_2 solution. The amount of SO_2 removed was calculated by integrating the curves of outlet SO_2 concentration with time. Breakthrough occurred when the outlet SO_2 concentration was 100 ppm.

3 Results and discussion

3.1 Physicochemical properties of prepared activated carbons

3.1.1 Texture properties

Table 1 contains the texture properties of the prepared activated carbons, including the BET surface area, total pore volume and average pore radius. When metal oxides were added at 2 wt%, the texture properties of modified activated carbon did not change significantly. The surface area and pore volume for the AC-Co2, AC-Ni2, and AC-Cu2 samples decreased slightly, and the surface area of AC-V2 was more developed relative to AC. At a loading rat of 2 wt%, the surface area increased in the following order: AC-Co2 < AC-Cu2 < AC-Ni2 < AC-V2. When the loading ratio increased to 5 wt%, the surface area and pore volume of all modified activated carbons decreased considerably, especially for AC-Ni5. However, AC-Co5 had a higher surface area (641 m^2/g) and total pore volume (0.420 cm^3/g) than that of AC (565 m^2/g and 0.380 cm^3/g).

The dosage of metal oxides significantly affected the development of texture properties of activated carbon. Apparently, the metal oxide dose should not exceed 5 wt% when blending method is used to modify activated carbon. Using proper loading ratio of metals promotes the formation of specific porosity due to the reaction between the added metal oxides and the carbon substrate during carbon gasification process. However, excess addition of metal particles may promote aggregation and the formation of large crystals during preparation. This process would result in pore blockage and surface area decrease (Nguyen-Thanh and Bandosz 2003; Lee et al. 2002).

3.2 Surface functionalities

XPS analysis was employed to investigate the surface functional groups of prepared samples. The C1s spectra of the activated carbon with and without modification are provided in Fig. 1. The C1s binding energy (BE) values for the modified activated carbon were similar to those of blank activated carbon, which suggested carbon properties did not significantly change after modification. All modified activated carbon had four components with BE value of approximately 284.6, 285.7, 287.6 and 289.4 eV. These BE values were assigned to C–C from graphitic carbon, C–O from phenolic etheric or alcoholic carbon, C=O bonds from carbonyl carbon and COOH bonds from carboxylic or lactonic carbon, respectively. However, difference in the functional groups concentrations of the activated carbons were not pronounced in the XPS spectrums, potentially due to the test limitations of this analytical method. Thus, FTIR was used to determine the development of the surface functional groups after metal addition.

As shown in Fig. 2, the FTIR spectra were similar for all carbon samples, which indicated the presence of similar functional groups on the carbon surface. This result agreed with the result obtained from XPS analysis. Broad peaks at approximated 3,400 cm^{-1} were assigned to the O–H stretching vibration of the hydroxyl functional groups (including hydrogen bonding) (Namasivayam and Kavitha 2006). Intensity increments in this position were observed for the Co, Cu and V modified activated carbons, which suggested a possible hydrogen-bonding interaction between the surface hydroxyl groups and the loaded metal oxides (Baltrusaitis et al. 2006). A band occurred at approximately 3,700 cm^{-1} in the AC-Co2, AC-Ni2 and AC-V2 samples. This band was due to the presence of hydroxyl groups that were coordinated to one metal atom (Rochester and Topham 1979). However, no peak in this area was detected in the 2 wt% CuO modified carbon sample. The band at 1,630 cm^{-1} was likely resulted from the C=O stretching vibration of different functional groups, including quinones and lactones (Sabio et al. 2004). Adsorptions due to C–O vibrations occurred between 1,300 and 900 cm^{-1}. The intense band at approximately 1,100 cm^{-1} was attributed to the C–O stretching of ether, ester, alcohol and phenol (Cain et al. 2010). The intensity

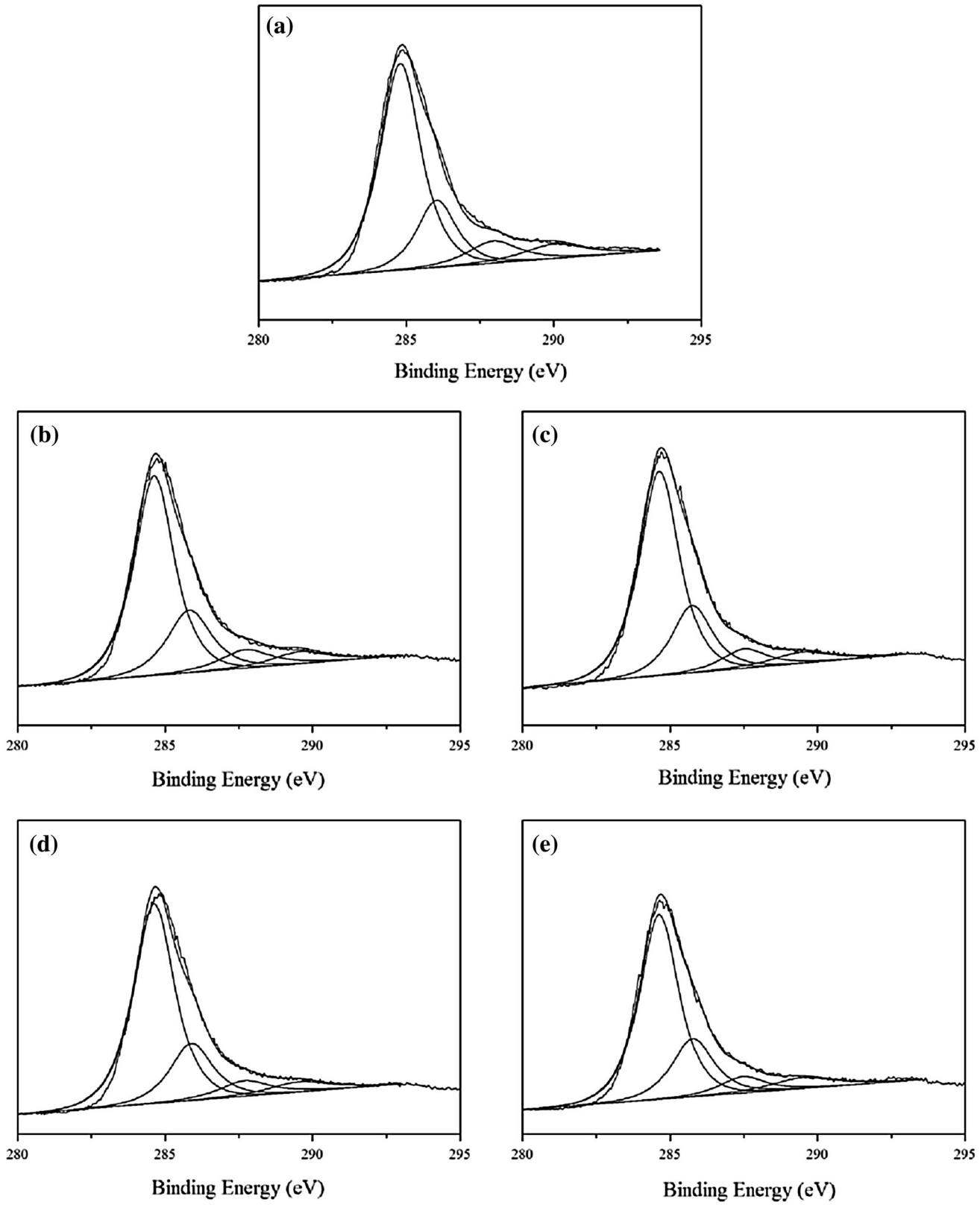

Fig. 1 The binding energy patterns of C1s for AC (**a**), AC-Co2 (**b**), AC-Ni2 (**c**), AC-Cu2 (**d**), AC-V2 (**e**)

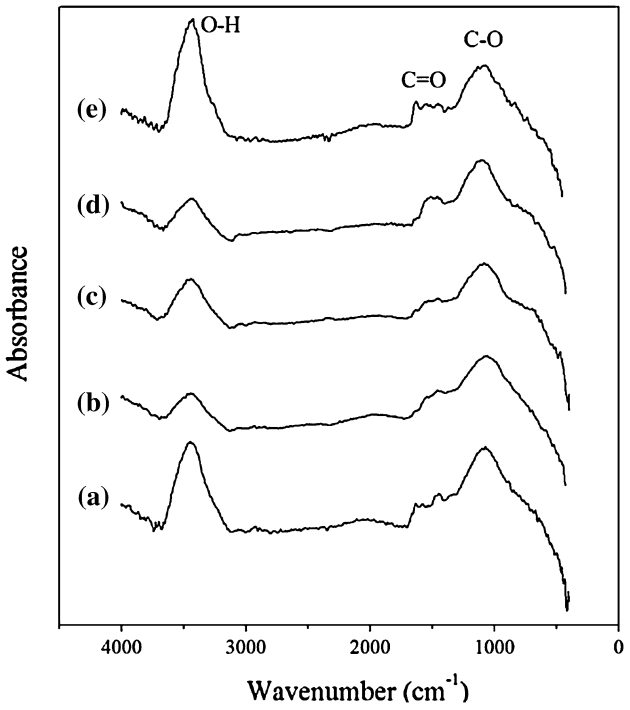

Fig. 2 Fourier-transform infrared spectra of prepared activated carbons: **a** AC; **b** AC-Co2; **c** AC-Ni2; **d** AC-Cu2; **e** AC-V2

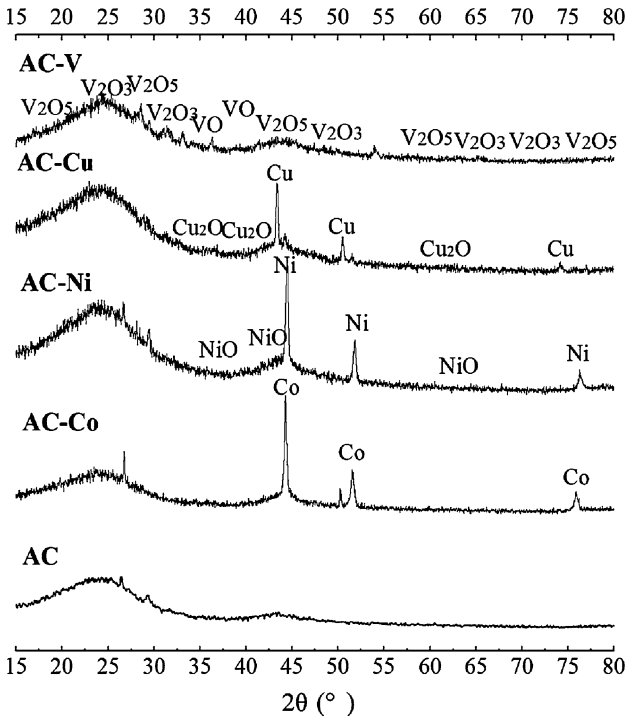

Fig. 3 X-ray diffraction patterns of blank activated carbon and modified activated carbon with the loading ratio of 2 wt%

Table 2 BA and DPG adsorption capacities of blank activated carbon and 2 wt% metal modified activated carbons

Activated carbon	BA[a] (mmol/g)	DPG[b] (mmol/g)
AC	0.286	0.010
AC-Co2	0.302	0.049
AC-Ni2	0.410	0.113
AC-Cu2	0.528	0.126
AC-V2	0.323	0.197

[a] Benzoic acid adsorbed from its alcoholic solution

[b] Diphenylguanidine adsorbed from its alcoholic solution

of these bands was enhanced after the addition of metal oxides, especially for the Cu, Ni and V modified carbons. This result indicated that these additives promoted the generation of oxygenated functional groups during their reaction with carbon in the activation process. According to previous research, the evolution of COO functional groups (e.g., carboxyl) makes activated carbons to be more acidic, while the CO functional groups (e.g., carbonyl) are often classified as basic groups (Balwant and Bansal 1964).

Furthermore, the BA and DPG adsorption capacities were evaluated to identify the basic and acidic active sites on activated carbon, respectively (Table 2). For all metal modified activated carbon, both basic and acidic active sites increased, which indicated the formation of additional surface functionalities. This finding corresponded with the FTIR results (Fig. 2). Some investigations have pointed out that the SO_2 adsorption process is favored by a high content of basic active sites on the surfaces of carbon materials (Li et al. 2001). However, the formation of surface acidic groups lessens the extent of such process (Davini 1989). In this study, the addition of transition metals was not able to destroy surface acidic sites at high temperature, in contrast with results from previous studies (Davini 2002). However, the concentration of basic active sites was much higher than acidic sites on activated carbon after metal addition by blending method. Thus, it was deduced that the considerably higher basic functional group content could be helpful for SO_2 removal, despite the increasing number of acidic sites.

3.3 Metal phases

The chemical compositions of the samples were examined by XRD. Figure 3 contains the XRD patterns for AC, AC-Co2, AC-Ni2, AC-Cu2 and AC-V2. For all samples, broad peaks were observed at $2\theta = 24°$ and 44°, which corresponded to those of amorphous carbon structures. In addition, diffraction peaks for SiO_2 at $2\theta = 26.6°$ were detected in all samples and were derived from the carbon char. The XRD pattern from AC-Co2 contained three peaks at $2\theta = 44.3°$, 51.5° and 75.9° (JCPDS 15-0806), which were ascribed to metallic cobalt particles (Chu et al. 2011;

Li et al. 2010). They could have been reduced completely at this high temperature during activation process when the Co species was presented on the surface of the carbon supports. Regarding AC-Ni2, diffraction peaks assigned to Ni were observed at $2\theta = 44.5°$, 51.8° and 76.4°, which (JCPDS 70-1849) (Qin et al. 2008). Except for the presence of metallic nickel, the reduction of Ni_2O_3 also caused the formation of NiO, with the reflection at 37.3°, 43.3° and 62.9° (JCPDS 47-1049) (Wu et al. 2011). For the 2 wt% CuO modified activated carbon, diffraction peaks located at 43.4°, 50.05° and 74.1° (JCPDS 85-1326) for the presence of Cu and at 36.7°, 42.5°, 61.9° and 73.9° (JCPDS 05-0667) for Cu_2O (Kobayashi et al. 2009). This result indicated that Cu and its oxides coexisted on the modified activated carbon. Compared to other samples, more diffraction peaks were observed for AC-V2, including V_2O_3 (JCPDS 34-0187), V_2O_5 (JCPDS 45-1074) and VO (JCPDS 65-4054). This result occurred because that vanadium species have significant mobility on certain oxide surfaces. And at relatively high concentrations, it is potentially easier for the vanadium species to agglomerate (Gao et al. 2011; Guo et al. 2009).

XPS analysis was conducted for further clarifying the catalytically active species of the metal additives on the modified activated carbons. It is known that the information depth of XPS test is only about 3 nm in general, hence the oxidized metals may cover the activated carbon surface and results in metals with other chemical states unexposed and undetectable by XPS test. For this reason, in this experiment, XPS analysis with the Ar^+ ion etching procedure was also performed on all metal loaded activated carbons, which was reported to be an effective way to extend the depth of the XPS analysis (Mutel et al. 1995; Paparazzo 1986). The XPS metal spectra of all 2 wt% metal loaded activated carbon samples with and without the Ar^+ etching procedure are exhibited in Fig. 4. It can be seen from Fig. 4, without etching with Ar^+ ions, the Co $2p_{3/2}$ peak around 780.7 eV was observed in sample AC-Co2 due to the presence of Co^{2+} (Gautier et al. 1997). For AC-Ni2, the Ni $2p_{3/2}$ BE was 854.4 eV, which was characteristic of Ni^{2+} in NiO (Roh et al. 2001). The strong shake-up line located at 860.8 eV belongs to Ni^{2+} species (Wang and Ozkan 2005). For 2 wt% CuO modified activated carbon, the Cu $2p_{3/2}$ was composed of two components at 933.7 and 942.0 eV, which indicated that the chemical state of copper is Cu^{2+} (Sinapi et al. 2002; Guo et al. 2011). The V 2*p*3/2 peak occurred at 517.5 eV, which was assigned to V^{5+}. Single peaks at approximately 521.8 eV were reported to result from the reflection of V_2O (Kónya et al. 2004). And with the Ar^+ etching process (Fig. 4b), peaks at 778.7 and 853.1 eV were detected for sample AC-Co2 and AC-Ni2, which was due to the presence of metallic Co and Ni (Hammond and Winograd 1977; Wang 1998). This is in good agreement with the results obtained by XRD analysis (Fig. 3). For sample AC-V2, the V2*p*3/2 peak was located around 515.4 eV, which was associated with the presence of VO_2 (Rao et al. 1979). The Cu 2*p*3/2 BE was found around 933.0 eV, which could be attributed to Cu(0) and Cu(I) (Aravinda et al. 2002; Hudak et al. 1990). Same result was also showed in XRD spectra.

By Combining the XPS and XRD results, reductions in the oxidation state were observed for all modified activated carbon, which occurred because of the blending method that was used in this study (one-step activation process). When heated at 900 °C with carbon materials in a CO_2 atmosphere these metal oxides were decomposed and then potentially reduced to a lower and more stable oxidation state during their reaction with the carbon substrate. For the AC-Co2, AC-Ni2 and AC-Cu2 samples, some of the additives were completely reduced to their metallic state and coexisted with metal oxides on the carbon surface. Four types of metal species, including V_2O_5, V_2O_3, VO and V_2O were formed on the carbon surface in the AC-V2 sample. These reduced state and intermediate state metal species are reported to be the primary active species for SO_2 removal due to their ability to change electron valence (Li et al. 2009).

3.4 Desulfurization activity tests

Figure 5 presents the SO_2 breakthrough capacity of activated carbon at different loading ratios (0–10 wt%). The sulfur capacity of blank activated carbon from walnut shells was high (123.8 mg/g), which suggested that walnut shells are good candidate as raw material for producing activated carbon. For carbon samples that were modified with CuO, Ni_2O_3 and V_2O_5, respectively, the sulfur capacity increased as the loading ratio increased from 0 to 2 wt% and decreased as the loading ratio increased above 2 wt%. This phenomenon was more evident for the V_2O_5 modified activated carbon. Compared with sample AC-V2, the sulfur capacity decreased by 56.6 % when the V_2O_5 ratio increased to 10 wt%. However, the desulfurization performance of AC-Co did not significantly change with different doses.

Furthermore, the best desulfurization performance for all modified activated carbon occurred at a loading ratio of 2 wt% for all modified activated carbon (Fig. 5). The sulfur capacities of AC-Co2, AC-Ni2, AC-Cu2 and AC-V2 were 133.3, 147.5, 172.4 and 181.2 mg/g, which were 7.7, 19.1, 39.3 and 46.4 % higher than the AC sulfur capacity, respectively. Vanadium appeared to be the one which most favors SO_2 sorption onto the carbon matrix. It has been reported that the catalytic activity of V is higher than that of the other metal oxides, such as Co, Ni and Cu (Gao et al. 2011).

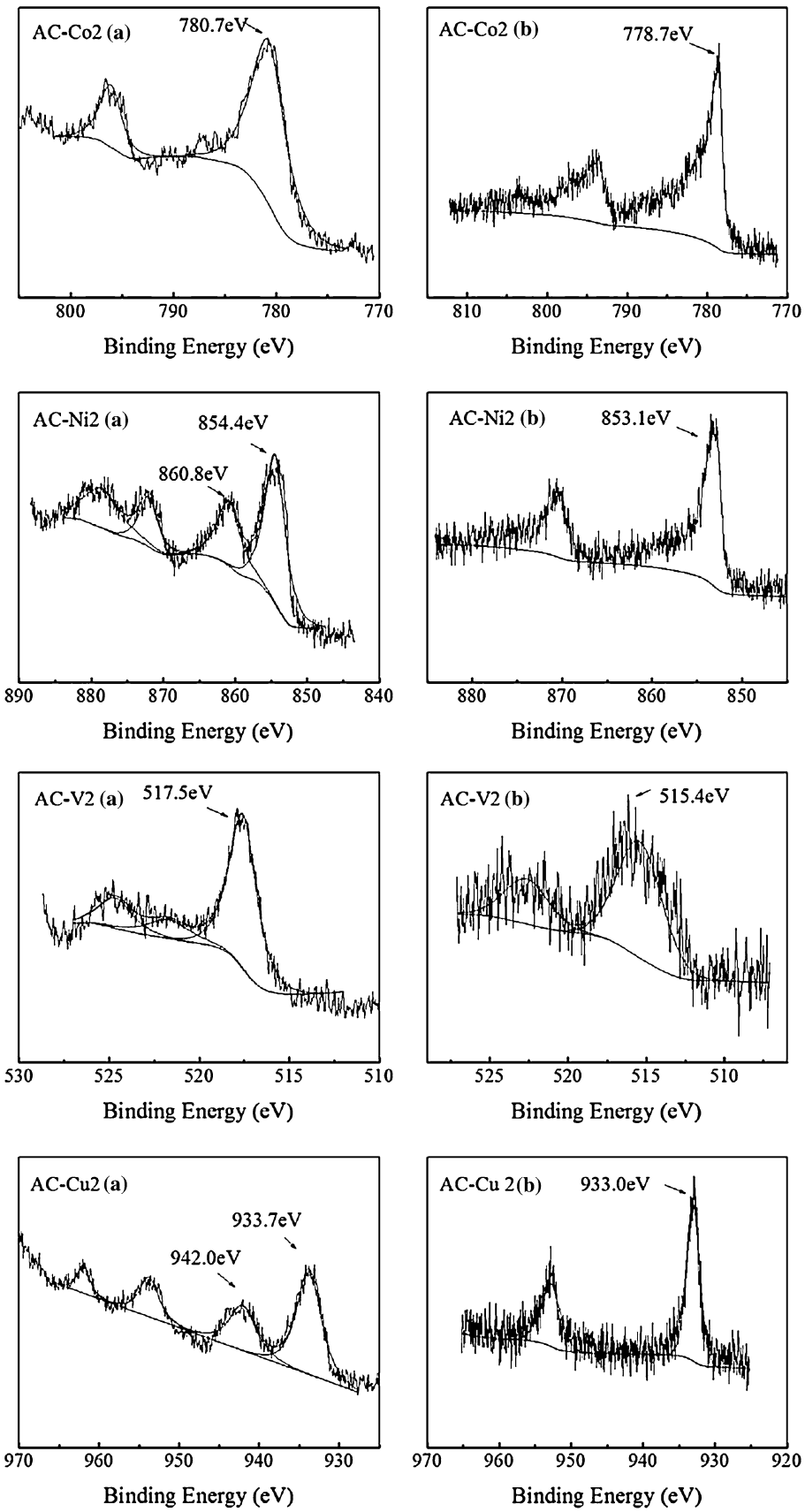

Fig. 4 Metal spectra for the different metal modified activated carbons **a** without and **b** with the Ar^+ etching procedure

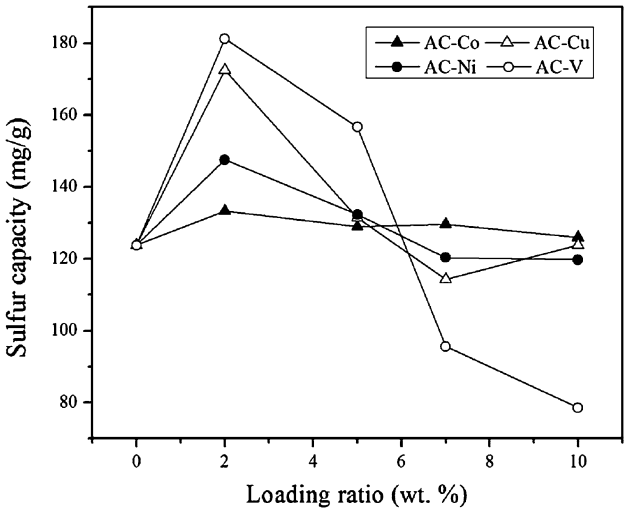

Fig. 5 Breakthrough sulfur capacities of all samples (with the loading ratio of 0, 2, 5, 7, 10 wt%)

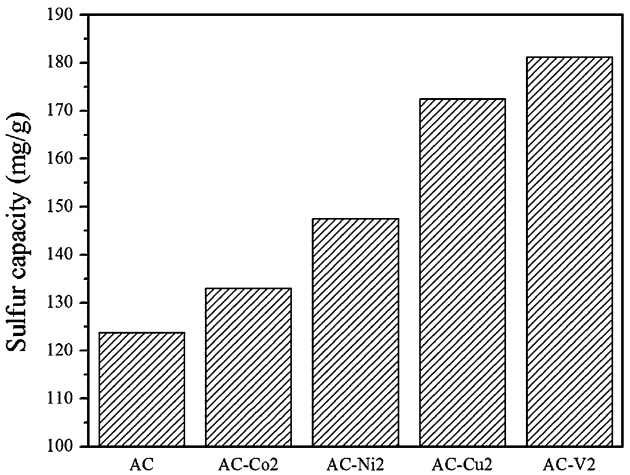

Fig. 6 Breakthrough sulfur capacity of 2 wt% metal modified activated carbon

Several factors can affect the removal performance of activated carbon for SO_2, including the specific surface area, pore-size distribution, pore volume, surface charge, presence of surface functional groups and catalytic activity of the metal species on the carbon surface. As shown in Table 1, the surface area and pore volume decreased considerably the loading ratio of the activated carbon exceeded 5 wt%. This result partially explained the significantly lower sulfur capacities of modified activated carbon with greater metal ratios because higher surface area and total pore volume positively affect SO_2 removal by carbon materials. For the 2 wt% metal modified activated carbons, the change of surface area and pore volume was not evident. Thus, the development of texture properties was not the main reason for their better desulfurization performance. It is also noticed that metal addition to activated carbon improved the generation of oxygenate functional groups on the carbon surface (Table 2). The increment of basic functional groups is beneficial for the SO_2 adsorption process on activated carbon due to the binding affinity. For example, AC-Cu2 possessed the highest basic functional group content and thus exhibited good desulfurization activity (Fig. 6).

Furthermore, the catalytic activities of the metal species resulted in improved desulfurization performance in the modified activated carbon. The oxidation state of the added metal oxides was partly reduced during carbon activation (Figs. 3, 4). In the oxidation catalytic reaction, the gaseous oxygen is first absorbed onto these reduced and intermediate state metal species and converted into the lattice oxygen. Active metal oxides with much higher catalytic activity were then formed by the reaction between the reduced and intermediate state metal species and the lattice oxygen atoms (Doornkamp and Ponec 2000). For example, for AC-V2, V^{3+}, V^{2+} and V^{1+} species coexisted on the carbon matrix after activation. These vanadium species would be oxidized by O_2 to active V_2O_5, which possesses a much higher catalytic activity for SO_2 than V_2O_5 (Li et al. 2009). Similar reactions occurred to form active metal oxides in the AC-Co2, AC-Ni2 and AC-Cu2 sample. Next, these active metal oxides reacted with SO_2 in the desulfurization system to formed SO_3. Specific mechanism can be described as follows:

$$MO_{x-n} + O_2 \rightarrow MO_{x-n} + O^{2-}(\text{lattice})$$

$$MO_{x-n} + O^{2-}(\text{lattice}) \rightarrow MO_x$$

$$MO_x \rightarrow MO_{x-n} + O\ (\text{ads})$$

$$SO_2(\text{ads}) + O\ (\text{ads}) \rightarrow SO_3(\text{ads})$$

This process was followed by H_2SO_4 generation with H_2O. The resulting metal species in their low oxidation state would be oxidized by O_2 in the desulfurization system to form active metal oxides again. It can be seen that this catalytic cycle depends on the change between chemical valences of the metal species. The complex metal species component in AC-V2 could partially explain its higher sulfur capacity compare to the other metal modified activated carbons.

The desulfurization capacity changed greatly when different transition metal oxides were used for activated carbon modification with blending method (Fig. 5). This is related with the variable nature and reaction mechanism of these metals themselves. When an additive dosage of 2 wt% was used, the AC-V2 and AC-Cu2 samples presented a higher SO_2 removal activity. This finding suggested that these expensive additives could be replaced with less expensive mineral ores or industrial solid wastes

that contain vanadium/copper to produce novel and inexpensive catalysts with high a desulfurization activity.

4 Conclusions

Walnut shell activated carbon was modified with transition metals (Co_2O_3, Ni_2O_3, CuO and V_2O_5) by blending method. At the optimal dosage of 2 wt%, the sulfur capacities of the Co, Ni, Cu and V loaded samples and the blank activated carbon were 133.3, 147.5, 172.4, 181.2 and 128.3 mg/g, respectively. The improvement of sulfur capacity mainly resulted from the additional basic functional groups that were generated after modification and the high catalytic activities of the active metal oxides that were formed during the desulfurization process.

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