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# Preparation of $\gamma$-$Al_2O_3$ sorbents loaded with metal components and removal of thiophene from coking benzene

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**Abstract** Series sorbents of Cu, Zn, Ni, Ce and Ag metal components supported on $\gamma$-$Al_2O_3$ carrier for removing thiophene from benzene were prepared by conventional and ultrasound-assisted incipient-wetness impregnation method. The static adsorption experiments were carried out in the thiophene-benzene solution with thiophene concentration of 500 mg/L. The results show that the desulfurization activity of all $\gamma$-$Al_2O_3$ sorbents modified by different metal components obviously increase, among which the sorbent modified by silver nitrate has the best performance. The active components of sorbents from Cu, Zn, Ni, Ce nitrates loaded on $\gamma$-$Al_2O_3$ carrier are their oxides. Besides $Ag_2O$, the products of silver nitrate thermal decomposition in sorbent prepared still have $Ag^0$ and Ag–O–Al species. The assistant ultrasound in the process of sorbent preparation can not only shorten the impregnation time, but also enrich the pore structure of sorbent and improve the size and distribution of the Ag species, which is favorable to the removal of thiophene from benzene. The desulfurization capacity of sorbent changes with the Ag content loaded. The sorbent with 15 % quality content of Ag prepared by ultrasound-assisted impregnation method has the highest desulfurization efficiency. It could reduce the thiophene concentration to 1.7 mg/L from 500 mg/L at room temperature and ambient pressure, with the desulfurization efficiency of more than 99 %, when the ratio of sorbent to solution was 1:4 (g/mL).

**Keywords** Thiophene · Benzene · Ultrasound · $\gamma$-$Al_2O_3$ · Adsorption

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## 1 Introduction

Benzene is an important chemical feedstock, mainly for the synthesis of styrene, phenol, chlorobenzene, resins, pharmaceuticals, rubber and other products. Pure benzene mainly comes from petrobenzene and coking benzene. With the rapid development of the coking industry, a large number of coking benzene is produced. But there is about 0.2–1.6 % thiophene in coking benzene, which may result in the catalyst poisoning and environmental pollution, so the further utilization of benzene is largely limited (Song 2003). At present, there are many methods for the removal of thiophene. Among those, adsorptive method has a great application potential, which can operate at ambient temperature and pressure and possesses the advantages of smaller equipment corrosion, less environmental pollution, lower operating costs, recovery of thiophene, and so on (Muzic et al. 2010). The sulfur capacity, selectivity and recyclability of sorbent are the key factors in the operation of this technique. There are many studies about the sorbents to removing thiophene, such as metal oxides (Larrubia et al. 2001; Srivastav and Srivastava 2009), zeolites (Yang et al. 2003), active carbon (Delitala et al. 2008), and their metal modified materials. But most of them are focus on the desulfurization of liquid fuel. Whereas the properties required sorbent for the removal of thiophene from coking benzene and liquid fuel are different, because of the existence of the competitive adsorption between aromatic compounds and thiophene (Hernández-Maldonado and Yang 2003, 2004).

$\gamma$-$Al_2O_3$ is usually used as the sorbent carrier for its characteristics of large surface area, good thermal stability, cheap and easy to get and so on (Prins et al. 1989), and some metals were selected as the active component because they can enhance the thiophene adsorption (Erickson 2003). Incipient-wetness impregnation method is a good quantitative loading method, but the load of active component on the carrier is not very uniform. Ultrasound may change the phase equilibrium relationship, increase the mass transfer rate between phases, and so as to promote the impregnation of active components on carrier (Simona and Gervasini 2000). Consequently, $\gamma$-$Al_2O_3$ was selected as the sorbent carrier and different metal nitrates were used as the precursors of active components, which was loaded by incipient-wetness impregnation method in this paper. At the same time, the ultrasound was introduced during impregnation to improve the sorbents' properties. The effect of active components and ultrasound were mainly discussed.

## 2 Experimental

### 2.1 Preparation of sorbents

Incipient-wetness impregnation method: The $\gamma$-$Al_2O_3$ powder with the particle size of 0.177–0.125 mm (80–120 mesh) was dried in an oven at 120 °C for 4 h to remove the water adsorbed on its surface. Then, it was impregnated in nitrate solution with a predicted volume for sever hours, dried in an oven at 100 °C for 2 h, calcined in Muffle at 500 °C for 4 h. The sorbent prepared was marked with SxM, where M means the active component, $x$ means the amount of the active component.

Ultrasound-assisted impregnation method: The above $\gamma$-$Al_2O_3$ dried was impregnated in nitrate solution in an ultrasound cleaner with the ultrasonic power of 50 W. Other preparation conditions are the same as the above method. The sorbent prepared was marked with SxMU, where M means the active component, x means the amount of the active component, and U means the ultrasound assistant.

### 2.2 Activity evaluation of sorbents

In these experiments, 1.00 g sorbent was put in a 4.00 mL ampule bottle containing 500 mg/L thiophene-benzene solution at room temperature for 24 h, which was considered that it had reached the adsorption quasi-equilibrium. The concentration of thiophene in the solution was analyzed by gas chromatography with the flame photometric detector (GC-FPD), and the desulfurization efficiency ($\eta$) was calculated as follows.

$$\eta = \frac{c_0 - c}{c_0} \times 100\ \%$$

where, $c_0$ is the initial concentration of thiophene in the solution (mg/L); $c$ is the concentration of thiophene in the solution (mg/L) when it reached the adsorption quasi-equilibrium.

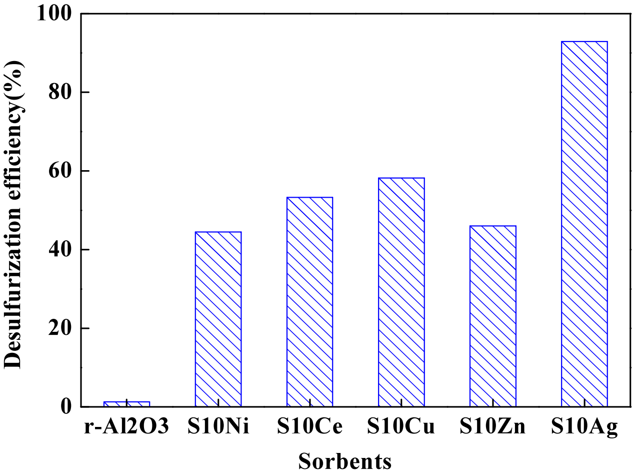

**Fig. 1** Efficiency of the sorbents with different metal components removing thiophene from benzene

### 2.3 Characterization of sorbents

The structure of sorbent was characterized by X-ray diffraction (XRD) apparatus of Rigaku D/max-rB (Rigaku, Japan) at a scanning rate of 5°/min from 10° to 80° with Cu-$K_\alpha$ radial ($\lambda = 0.154$ nm), 40 kV tube voltage and 100 mA tube current. The surface area, pore volume and pore size distribution were measured by SORPTOMATIC 1900SERIES (Micromeritics, USA) apparatus using $N_2$ adsorption according to the BET and BJH models. The surface morphology of the sorbent was characterized by JSM-6700F Scanning Electron Microscopy (JEOL Ltd., Japan) apparatus with accelerating voltage of 10 kV. In order to investigate the forms of silver in the sorbent, the binding energy of Ag $3d_{5/2}$ on its surface was determined by X-ray photoelectron spectroscopy (XPS) using ES-CALAB250 spectrometer (Finnigan, USA) equipped with Al $K_\alpha$ source. The spectrum was taken in high vacuum of $10^{-7}$ Pa. And the calibration was carried out to the main C 1$s$ peak at 284.6 eV.

## 3 Results and discussion

### 3.1 Effect of the metal component on the sorbent

Figure 1 shows the adsorption results of the sorbents prepared by incipient-wetness impregnation method, with the active component content of 10 %. It can be seen that $\gamma$-$Al_2O_3$ has little desulfurization ability, and it plays mainly the role of carrier. The desulfurization ability of the metal component loaded sorbents is all improved significantly, among which the sorbent modified in silver solution has the best desulfurization performance. The XRD patterns of the above sorbents are shown in Fig. 2. It could be easily concluded that the active components of the sorbents are $Ag^0$,

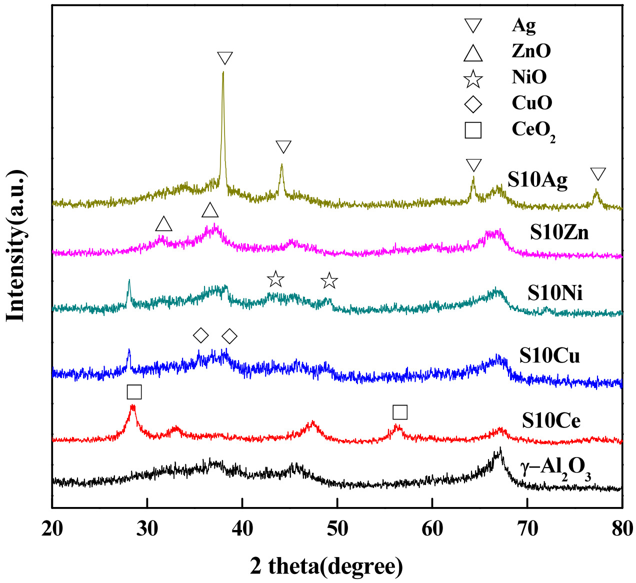

**Fig. 2** XRD diffraction patterns of sorbents with different metal components

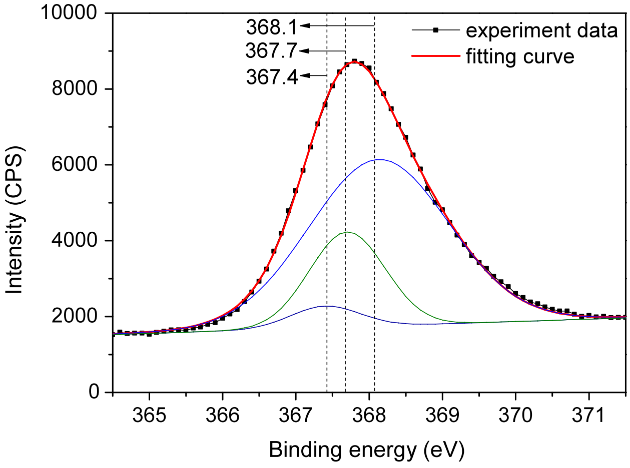

**Fig. 3** XPS spectrum of the core level of Ag $3d_{5/2}$ region recorded with S15AgU sorbent

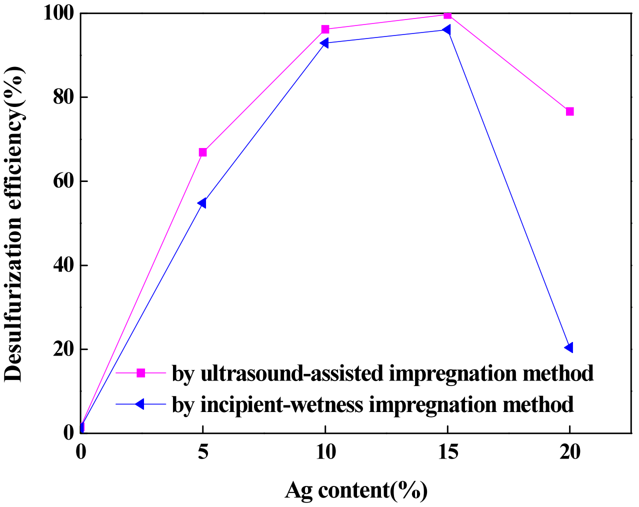

**Fig. 4** Effect of Ag content in sorbent on the thiophene adsorption (impregnated for 4 h)

ZnO, NiO, CuO, and $CeO_2$, respectively. From the literatures (Jackson et al. 1995; Chen and Zhang 2003; Kwon et al. 2005), it can be found that the thermal decomposition products of $AgNO_3$ are $Ag^0$, $NO_2$ and $O_2$ following the equation $2AgNO_3 = 2Ag + 2NO_2 + O_2$. But the sliver exits in three forms of $Ag^0$, $Ag_2O$ and Ag–O–Al species after loaded on the $\gamma$-$Al_2O_3$ support (Kannisto et al. 2009), their binding energy are 368.1 eV, 367.7 eV and 367.4 eV respectively (Schön 1973). Figure 3 shows the XPS spectrum of the core level of Ag $3d_{5/2}$ region recorded with S15AgU sorbent. According to the ratio of the area of the three peaks, it can be calculated that the molar ratio of $Ag^0$, $Ag_2O$ and Ag–O–Al species to the total silver is 82.33 %, 12.47 % and 5.20 % respectively. $Ag^0$, $Ag_2O$, $Ni^{2+}$, $Zn^{2+}$, $Cu^{2+}$, and $Ce^{4+}$ have free orbit outside the atomic nucleus to accept electron, which makes them belong to Lewis acid. In contrast, thiophene molecule has free electrons to provide, which makes it belong to Lewis base (Xue et al. 2005). Thiophene could be removed according to the interaction between thiophene and the active components. Among these Lewis acids, $Ag^0$ and $Ag_2O$ can be attributed to the soft acid, while $Ni^{2+}$, $Zn^{2+}$, and $Cu^{2+}$ are the intermediate acid, $Ce^{4+}$ is the hard acid (Ho 1975; Jeevanandam et al. 2005). According to the principle of "Hard and Soft Acid and Base"—hard likes the hard and soft likes the soft (Peatson 1963), $Ag^0$ and $Ag_2O$ has the strongest force with thiophene, because thiophene is the soft base. In addition, Ag–O–Al species should be also the main active component to remove thiophene. So the sorbent prepared by silver nitrate loaded on $\gamma$-$Al_2O_3$ is better than others.

### 3.2 Effect of the metal component content on the sorbent

Sorbents with different Ag contents were respectively prepared by conventional incipient- wetness impregnation and ultrasound-assisted impregnation method, the adsorption abilities of which are shown in Fig. 4. It can be seen that the desulfurization efficiency of sorbents increases with the increasing of Ag content. When the Ag content reaches up to 15 %, it tends to balance and then decreases with its continuous increase. This should be due to that active component is benefit for adsorption, but excessive amount of them may emerge agglomeration.

### 3.3 Effect of ultrasound assistant on the sorbent

From Fig. 4, it can be also found that the sorbents prepared by ultrasound-assisted impregnation method have better adsorption behavior than those prepared by incipient-wetness impregnation method. The desulfurization efficiency of the sorbent with 15 % Ag is nearly to 100 %. Figure 5 is the effect of impregnation time on thiophene adsorption of sorbents prepared by different methods. It can be seen that the desulfurization efficiency of the sorbents prepared by incipient-wetness impregnation method increases with the growth of impregnation time, and reaches to maximum after 4 h. The desulfurization efficiency of the sorbent prepared by ultrasound-assisted impregnation method is up to 99 % when the time is up to 0.5 h, and its variation is insignificant with the extension of impregnation time. The cavitation effect in ultrasound could increase the mass transfer rate between phases, so it could obviously shorten the impregnation time and improve the properties of sorbent.

In order to find the reason of the promote effect caused by the assistant of ultrasound, XRD, BET, and SEM were used to characterize the sorbents. From the XRD diffraction patterns of sorbents with different Ag content in Fig. 6, it is shown that the diffraction peak sites of sorbents prepared by different methods are identical, which illustrates that ultrasound has little effect on the existing form of the active component. However, the intensities of peaks from the sorbents prepared by ultrasound-assisted impregnation method are lower, and half-peak widths are wider than that of sorbents prepared by incipient-wetness impregnation method, which illustrates that ultrasound could make the active components disperse well so as to improve their desulfurization activity.

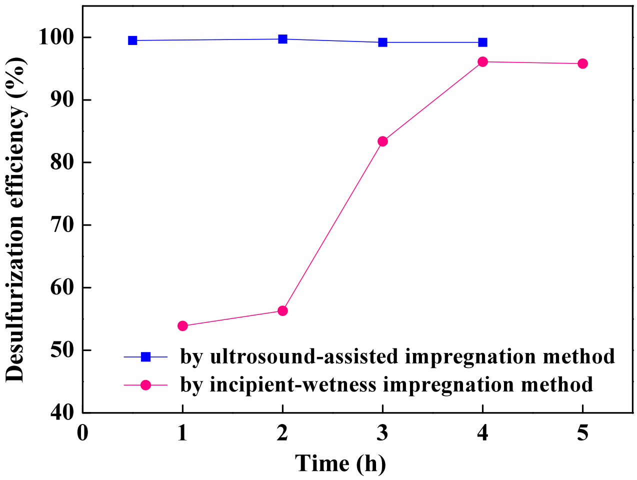

**Fig. 5** Effect of impregnation time on thiophene adsorption of sorbents prepared by different methods

Table 1 is the BET results of the sorbents, and the distribution curves of the pore size for sorbents were shown in Fig. 7. It can be found from Table 1 that the special surface area and pore volume of the sorbents prepared by ultrasound-assisted impregnation method are larger. This is because the cavitation effect of ultrasound can produce lots of bubbles, which will bring a big impact on the surface of the sorbents, after the cycle changes of growth-contraction (Bianchi et al. 1997, 2001). The enlargement of special surface area and pore volume provides a larger space for the load of active component, which is benefit for the adsorption of thiophene. From Fig. 7, it can be seen that the pore size distribution of the sorbents prepared by incipient-wetness impregnation method is almost the same as the carrier, but wider and bigger than that of the sorbents prepared by ultrasound-assisted impregnation method. This may due to that the active component is mostly loaded on the surface of sorbents prepared by incipient-wetness impregnation method, whereas ultrasound is benefit for the active component going into the internal channel to achieve uniformly loading.

Figure 8 is the SEM results of series sorbents. From the images, it can be seen that the particles of active component loaded on the sorbents prepared by ultrasound-assisted impregnation method are all smaller and more uniform. Because the high temperature and high pressure environment produced by the cavitation effect of ultrasound could provide the required energy for the formation of small particles and accelerate the precipitation nucleation rate for several orders of magnitude to decrease the sediment particle size thereby. Moreover, the high temperature and lots of bubbles produced by the cavitation effect of ultrasound can greatly

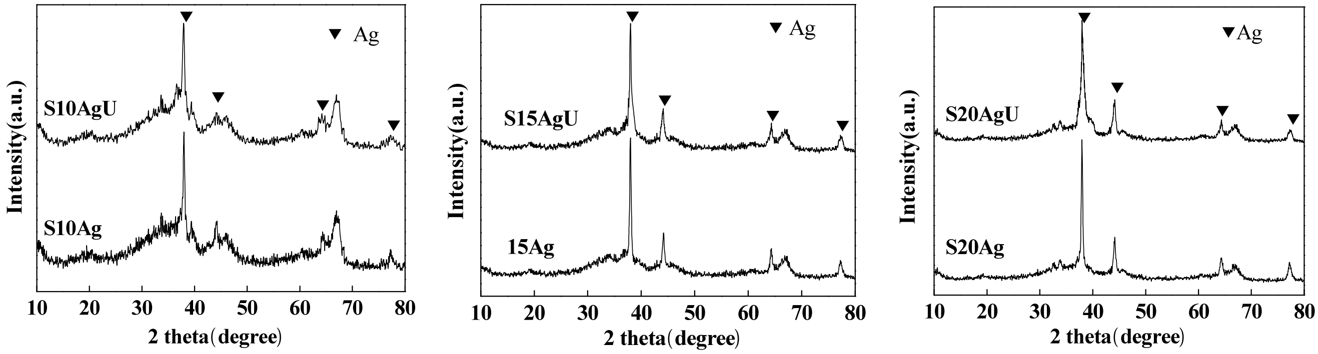

**Fig. 6** XRD diffraction patterns of sorbents with different Ag content

**Table 1** Pore structure parameters of sorbents prepared by different methods

| Samples | S5Ag | S5AgU | S10Ag | S10AgU | S15Ag | S15AgU | S20Ag | S20AgU |
|---|---|---|---|---|---|---|---|---|
| $S_{\mathrm{BET}}$ ($m^2\,g^{-1}$) | 145.70 | 185.56 | 131.47 | 172.69 | 132.06 | 160.24 | 119.49 | 115.90 |
| Pore volume ($cm^3\,g^{-1}$) | 0.18 | 0.26 | 0.17 | 0.25 | 0.15 | 0.18 | 0.15 | 0.23 |

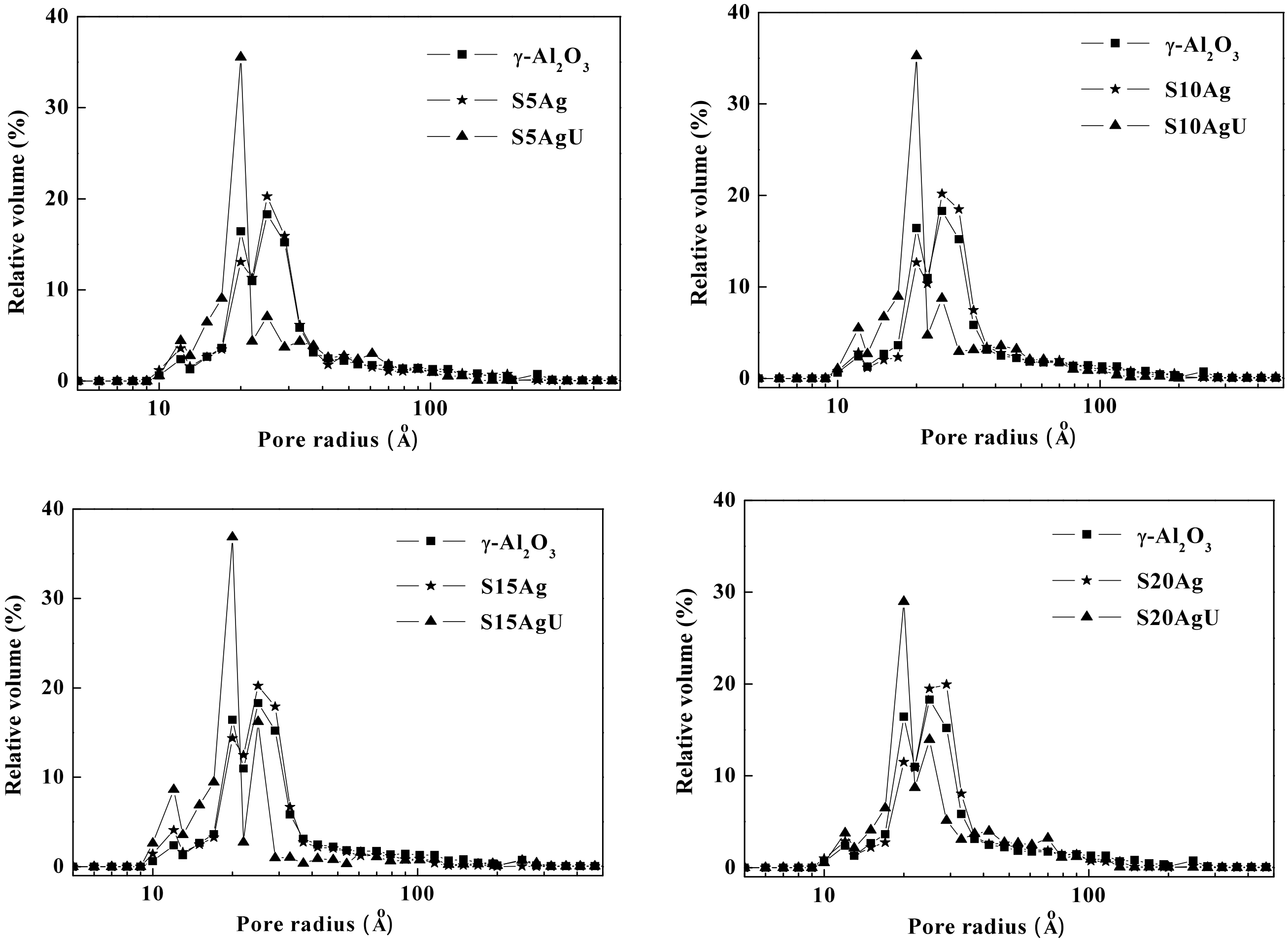

**Fig. 7** Distribution curves of the pore size for Ag/$\gamma$-$Al_2O_3$ series sorbents

reduce the specific surface free energy of crystal core, which may inhibit the coalescence and growth of the crystal. In addition, the shock wave and crushing effect generated by the ultrasound make the precipitation to be the uniform small particles (Jeevanandam et al. 2002). The smaller the particles of active component are, the more beneficial it is for adsorption due to the more active sites. It could also be found that when the Ag content is less than 15 %, there is little agglomeration of metal component; while when the Ag content is up to 20 %, there is significant agglomeration, which could reduce the utilization of the active component and block some of the channels. This may explain why the desulfurization efficiency of sorbent with 20 % Ag promptly decreases.

## 4 Conclusions

The sorbents prepared by Cu, Zn, Ni, Ce and Ag metal components supported on $\gamma$-$Al_2O_3$ carrier could effectively remove thiophene from benzene. The desulfurization ability of $\gamma$-$Al_2O_3$ is significantly improved after modificated by those metal components, among which the sorbent modified by silver nitrate has the best performance. The active components of sorbents from Cu, Zn, Ni, Ce nitrates precursor solutions are their oxides. For silver nitrate, the products of thermal decomposition in sorbent prepared contain $Ag^0$ and Ag–O–Al species besides $Ag_2O$. The content of active component affects the desulfurization ability of the sorbent and the desulfurization efficiency of sorbent increases with the

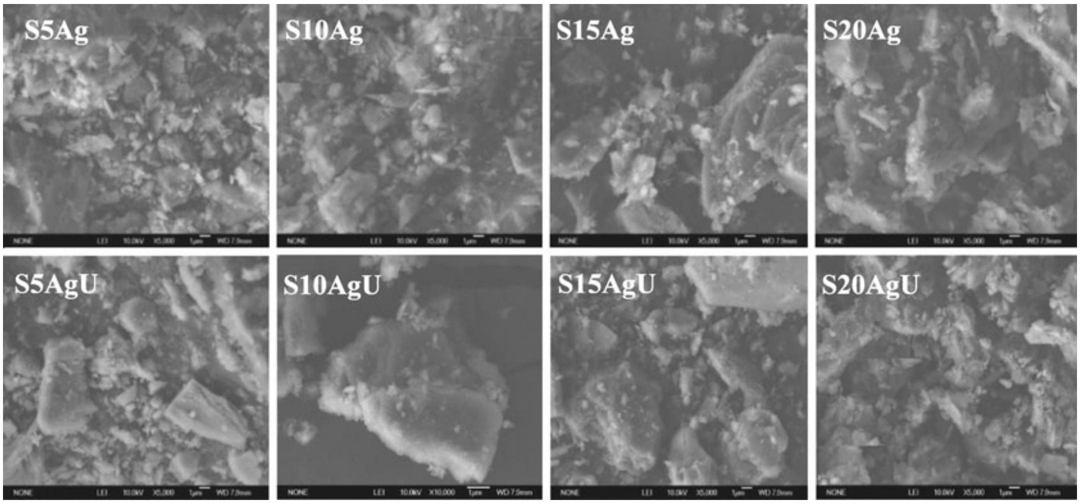

**Fig. 8** SEM results of series sorbents

increasing of Ag content. The capacity of SAgU series sorbent tends to balance with the Ag content up to 15 %, but decreases when the Ag content is 20 % due to agglomeration. Ultrasound could not only increase the desulfurization efficiency, but also shorten the impregnation time significantly, through improving the pore structure of sorbents and the particle size and distribution of active component, which are all of benefit to the adsorption of thiophene.

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