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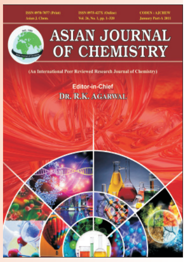

Adsorptive Removal of Thiophenic Sulfur Compounds Over Ag-Loaded Spherical Activated Carbon

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Silver-loaded spherical activated carbon (Ag-SAC) was synthesized by liquid phase ion exchange using phenolic weak acid cation exchange resin, carbonization and activation with CO_2. The adsorptive capacity and selectivity of Ag-SAC for thiophene (T), 3-methylthiophene (3-MT) and 2,5-dimethylthiophene (2,5-DMT) were investigated by the fixed bed adsorption experiments under ambient conditions. The results showed that the saturation capacities of Ag-SAC for T, 3-MT and 2,5-DMT were 0.733, 0.925 and 1.143 mg-S/g-A, respectively and the adsorptive selectivity of the adsorbent for different sulfur compounds followed the order: 2,5-DMT > 3-MT > T. The effects of toluene and cyclohexene on the adsorptive performance were also studied. The results indicated that the presence of toluene and cyclohexene led to a reduction of total saturation capacity by 57 and 33 %, respectively.

Keywords: Adsorptive desulfurization, Adsorptive selectivity, Ag-loaded, Spherical activated carbon, Thiophenic sulfur compounds.

INTRODUCTION

Recently, a few Chinese cities were blanketed in a thick haze, with people suggested to stay indoors and beginning to think about the reason and the harm of the haze. The main components of haze are SOx and NOx whose resource is mainly vehicle exhaust. In fact, sulfur in transportation fuels can not only be converted into toxic SOx leading to acid rain, but also poison catalysts treating vehicle exhaust[1]. In addition, liquid hydrocarbon fuels are ideal fuels for fuel cells thanks to their high energy density, safety for transportation and ease for storage[2]. However, the sulfur concentration should be reduced to less than 0.1 ppmw in order to avoid poisoning the catalysts in the electrodes of the fuel cells[3]. As a result, many countries and regions have established strict regulations to limit the sulfur concentration in the fuels. For instance, the maximum allowable sulfur content in automotive gasoline was 10 ppmw by 2010 in the EU and 50 ppmw by 2011 in China. With increasingly stringent environmental regulations, deep desulfurization of commercial fuels has become a more and more important research topic worldwide[4-6].

Nowadays, methods for deep desulfurization of liquid fuels mainly include catalytic hydrodesulfurization (HDS), chemical oxidation, adsorptive desulfurization, extractive desulfurization and biodesulfurization[7-11]. As the traditional method for desulfurization, hydrodesulfurization can efficiently remove thiols, sulfides and disulfides by catalytic reactions with hydrogen at high temperature (300-340 °C) and high pressure (3-7MPa)[12]. However, hydrodesulfurization leads to reduction of octane number and relative expensive operating costs, besides, thiophene derivatives are difficult to be removed by hydrodesulfurization[13]. Consequently, adsorptive desulfurization is regarded as a promising approach for deep desulfurization due to its ambient operating temperature and atmospheric pressure, low-energy consumption and the broad availability of adsorbent[14]. A kind of suitable adsorbents is the core of adsorption desulfurization. In general, various materials including the reduced metals, metal sulfides, metal oxides, activated carbons and zeolite-based materials are being studied as adsorbents[15-18].

In this paper, phenolic weak acid cation exchange resin was chosen as carbon precursor to prepare spherical activated carbon (SAC) and Ag-SAC and the adsorptive desulfurization of model fuels was conducted in a fixed bed system to study the adsorption of T, 3-MT and 2,5-DMT on Ag-SAC. The adsorptive capacity and selectivity for various sulfur compounds and the effects of toluene and cyclohexene on the adsorptive performance were investigated. According to the results of characterization and experiments, the adsorptive selectivity and mechanism were further discussed.

EXPERIMENTAL

The adsorbates, thiophene (T) (99 %), 3-methyl thiophene (3-MT) (98 %), 2,5-dimethyl thiophene (2,5-DMT) (98 %)

were purchased from Alfa Aesar (Tianjin) Chemical Co., Ltd.. Phenolic weak acid cation exchange resin (PR) used in this study was supplied by Anhui Sanxing Resin Technology Co., Ltd., China. Toluene, cyclohexene, $AgNO_3$ and *n*-heptane were all analytical reagents. All the compounds were used without further purification.

Preparation of adsorbents: Silver-loaded spherical activated carbon (Ag-SAC) was prepared by ion exchange of PR with $AgNO_3$ aqueous solution (0.2 M). The amount of silver in the ion exchange solution was equivalent to cation exchange capacity. After ion exchange for 24 h, the ion-exchanged resin was washed with sufficient deionized water until Ag^+ was undetected in the eluate. Silver-loaded spherical activated carbon was obtained after the ion-exchanged resin was dried in an oven, carbonized at 600 °C for 1h under a nitrogen flow and activated by CO_2 at 850°C for 2h at the flow rate of 50 mL/min. Spherical activated carbon without loading metal was obtained under the same conditions of carbonization and activation.

Characterization of adsorbents: The surface structure of the adsorbent was observed by JSM-6360LV scanning electron microscope (SEM). The phase of metal loaded on Ag-SAC was analyzed by D8 ADVANCE X-ray diffractometer. The BET surface areas and pore sizes of the samples were characterized by adsorption/desorption of N_2 at -196 °C by SSA-4300 surface area and porosimetry analyzer.

Model gasoline: The compositions of three different model gasoline samples (MG-I, MG-II and MG-III) in this work are listed in Table-1.

Fixed-bed adsorption/breakthrough experiments: Adsorptive desulfurization of the three model gasoline fuels was performed at 25 °C and under atmospheric pressure. The adsorbent was packed in a stainless steel column with a bed dimension of 8 mm i.d. and 200 mm length. The model fuels flowed up through the adsorbent bed at a liquid hourly space velocity (LHSV) of 4.5 h^{-1} and the effluent from the top of the column was collected periodically for analysis. The sulfur concentrations of various thiophenic compounds in the treated and untreated fuels were examined by a gas chromatograph (GC) equipped with flame photometric detector (FPD). In addition, the total sulfur concentrations were analyzed by WK-2D total sulfur analyzer.

RESULTS AND DISCUSSION

Characterization of adsorbents: The SEM photographs of Ag-SAC are shown in Fig. 1. As it can be seen in the Fig. 1, the Ag-SAC prepared in this study is spherical particles and has a certain degree of pore structure.

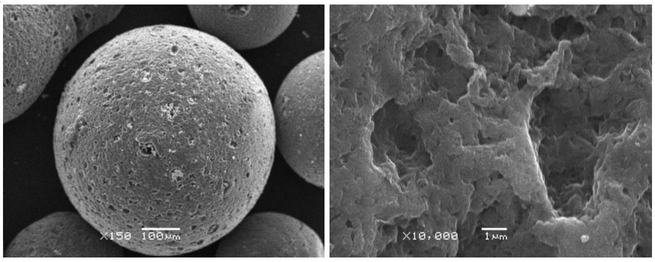

Fig. 1. SEM photographs of silver-loaded spherical activated carbon

The X-ray diffraction (XRD) spectra of the adsorbent samples are shown in Fig. 2. The broad peaks of 26° and 44° are the characteristic diffraction peaks of 002 and 010 crystal faces of carbon graphite crystallites, respectively. The sharp peaks of 38, 44, 65 and 77° are the characteristic diffraction peaks of elemental silver, indicating that Ag^+ is reduced into elemental state in the process of preparing.

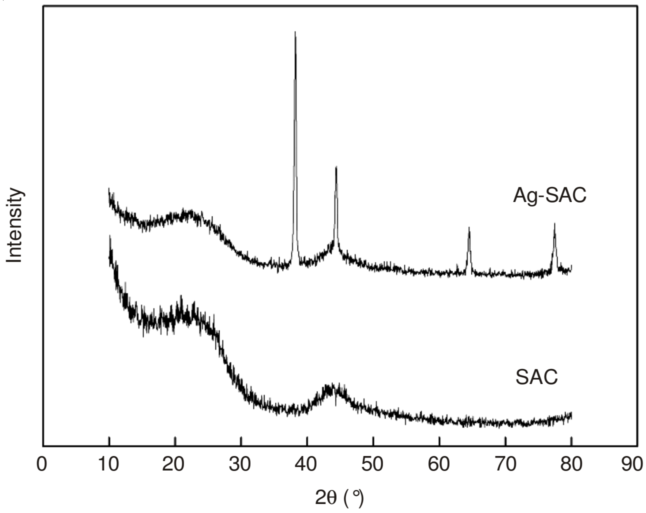

Fig. 2. XRD spectra of spherical activated carbon and silver-loaded spherical activated carbon (Ag-SAC)

TABLE-1
CONCENTRATION OF EACH COMPOUND IN DIFFERENT MODEL GASOLINE SAMPLES

Compounds	MG-I		MG-II		MG-III	
	Weight (%)	S (ppmw)	Weight (%)	S (ppmw)	Weight (%)	S (ppmw)
Thiophene	0.0258	98.4	0.0258	98.3	0.0259	98.6
3-MT	0.0303	98.8	0.0302	98.7	0.0300	98.1
2,5-DMT	0.0349	99.6	0.0347	99.1	0.0349	99.7
Toluene	—	—	25.00	—	—	—
Cyclohexene	—	—	—	—	25.00	—
n-heptane	99.9090	—	74.9093	—	74.9092	—

TABLE-2
BET SURFACE AREA AND PORE CHARACTERIZATION OF DIFFERENT ADSORBENTS

Adsorbents	BET surface area (m^2 g^{-1})	Pore volume (cm^3 g^{-1})	Pore size (nm)
SAC	283.54	0.254	1.79
Ag-SAC	210.47	0.183	1.74

The pore size distribution and the data of surface area and pore size of SAC and Ag-SAC are shown in Fig. 3 and Table-2, respectively. Compared with SAC, both the specific surface area and pore volume of Ag-SAC reduce. This may be because silver adhered to the surface and the pores lead to the collapse of the framework and blocking of the pores during the process of preparing.

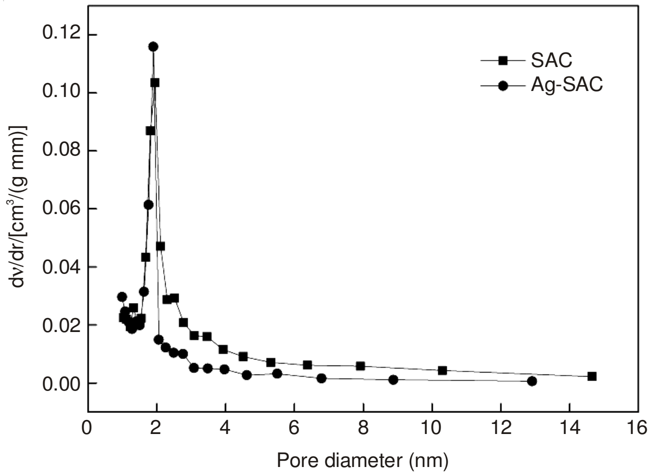

Fig. 3. Pore size distributions of SAC and Ag-SAC

Adsorptive performance for MG-I: The adsorptive capacity and selectivity of adsorbents for various sulfur compounds in different model gasoline fuels were investigated by the fixed bed adsorption experiments. The breakthrough curves of the thiophenic compounds were obtained by plotting the milliliters of the treated fuels per gram of adsorbent (mL/g) as a function of the C/C_0 value (a ratio of the effluent sulfur concentration to the initial sulfur concentration in the model fuels). The breakthrough curves of MG-I on SAC and Ag-SAC are shown in Figs. 4 and 5, respectively.

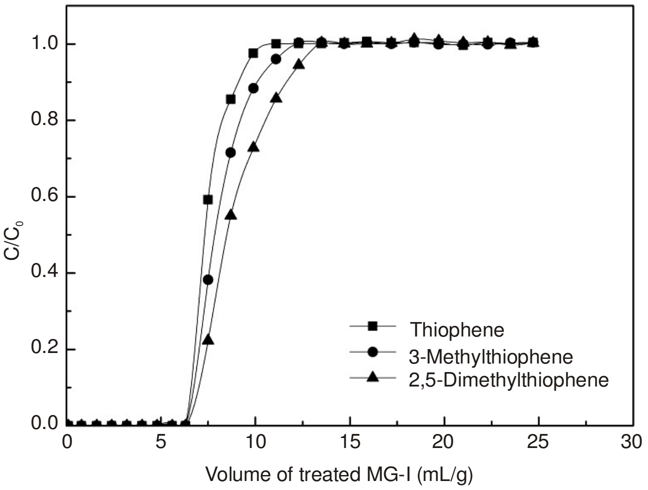

Fig. 4. Breakthrough curves of MG-I over SAC

It can be seen from Figs. 4 and 5 that there are relative significant changes in the desulfurization performance of MG-I on the two adsorbents. The saturation capacities of the three sulfur compounds (the milligrams of the treated sulfur per gram of adsorbent corresponding to the saturation point where C/C_0 is approximately equal to 1, mg-S/g-A) were used to be the standards of evaluation for adsorptive performance of adsorbents. The saturation capacities of various thiophenic compounds are calculated based on the breakthrough curves and listed in Table-3.

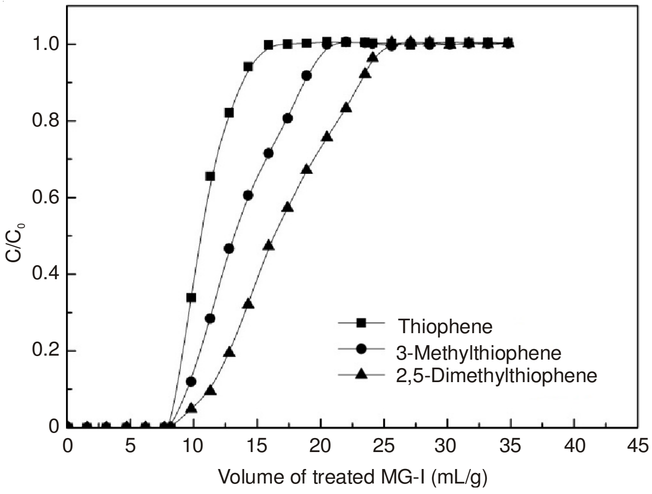

Fig. 5. Breakthrough curves of MG-I over Ag-SAC

According to Table-2, the pore size and BET surface area of Ag-SAC are smaller than that of SAC, but the total adsorptive capacities of Ag-SAC for MG-I in Table-3 are 1.7 times of the amount of SAC. The results show that the introduction of silver improves the adsorptive capacity, indicating that there should be the presence of other interactions between the thiophenic sulfur compounds and Ag-SAC apart from physical adsorption depending on BET surface area and the pore size. Song *et al.*[2] reported that thiophenic compounds can coordinate the metal through sulfur-metal interaction and π-electrons of unsaturated bonds. The reason why the adsorptive capacity of Ag-SAC improved is the interactions between thiophenic compounds and Ag.

In order to facilitate discussion of the adsorptive selectivity of the adsorbent for different sulfur compounds, a relative selectivity factor was applied in this study, which is defined as:

$$\alpha_i = \frac{q_i}{q_r}$$

where q_i is the saturation capacity of compound i and q_r is the saturation capacity of reference compound, thiophene. The calculated relative selectivity factors are shown in Table-4.

TABLE-3
ADSORPTIVE CAPACITY OF DIFFERENT ADSORBENTS FOR MG-I

Adsorbents	Saturation capacity (mg-S/g-A)			
	T	3-MT	2,5-DMT	Total
SAC	0.510	0.551	0.608	1.669
Ag-SAC	0.733	0.925	1.143	2.801

TABLE-4
RELATIVE SELECTIVITY FACTORS OF DIFFERENT THIOPHENIC SULFUR COMPOUNDS

Adsorbents	Relative selectivity factor of each compound		
	T	3-MT	2,5-DMT
SAC	1.00	1.08	1.19
Ag-SAC	1.00	1.26	1.56

TABLE-5
ADSORPTIVE CAPACITY OF MG-II AND MG-III OVER AG-SAC

Model gasoline	Saturation capacity (mg-S/g-A)			
	T	3-MT	2,5-DMT	Total
MG-II	0.367	0.398	0.441	1.206
MG-III	0.581	0.612	0.682	1.875

According to Table-4, the introduction of Ag also increases the relative selectivity, indicating that the intensity of the interaction between Ag and different thiophenic sulfur compounds are different. Ma *et al.*[19] calculated the electron density on the sulfur atom of different sulfur compounds and the values of T, 3-MT and 2,5-DMT are 5.689, 5.697 and 5.716, respectively. The relative selectivity factors of Ag-SAC for the three sulfur compound are consistent with the order and the three compounds have the same number of π-electrons,implying that the direct sulfur-metal interaction mainly controls the intensity of the interaction between Ag and different thiophenic sulfur compounds.

Effect of aromatic hydrocarbon and olefin: In order to further investigate the adsorptive performance of Ag-SAC, the adsorptive desulfurization of MG-II containing toluene and MG-III containing cyclohexene were conducted under the same experimental conditions. The breakthrough curves of MG-II and MG-III on Ag-SAC are shown in Figs. 6 and 7, respectively.

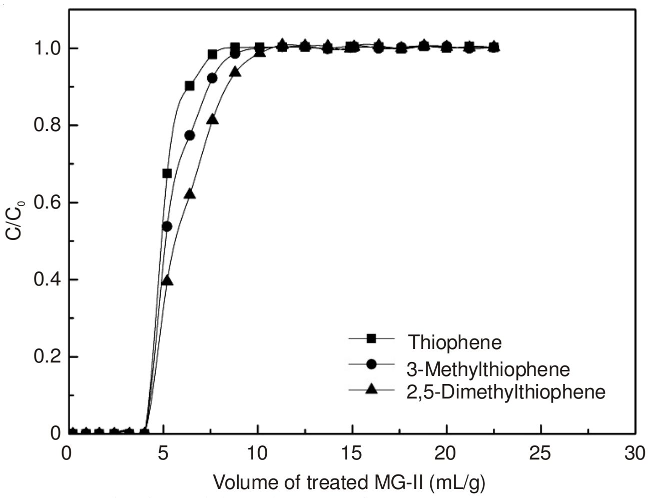

Fig. 6. Breakthrough curves of MG-II over Ag-SAC

The saturation capacities of various thiophenic compounds in MG-II and MG-III on Ag-SAC are calculated based on the breakthrough curves and shown in Table-5. Compared with the adsorptive capacities of Ag-SAC for MG-I, the adsorptive capacities for MG-II and MG-III lessen significantly due to the addition of toluene or cyclohexene. The total saturation capacities of Ag-SAC for MG-II and MG-III decrease by 57 % and 33 %, respectively. The results indicate that toluene and cyclohexene have competitive adsorption with thiophenic sulfur compounds on Ag-SAC and toluene shows stronger competitive performance than cyclohexene. Aromatics and olefins can interact with metal through π-electrons[20] so that they can compete for the active sites of the metal. The toluene molecule has a π-conjugated system involved six π-electrons and cyclohexene molecule has a pair of π-electrons, which means that toluene can have a stronger interaction with Ag than cyclohexene through π-electrons. After adding toluene and cyclohexene to the MG-II and MG-III separately, these molecules compete for the same active sites on the Ag-SAC, leaving less active sites for thiophenic sulfur compound molecules compared with MG-I. As a result, the adsorptive capacities of MG-II and MG-III on the Ag-SAC decreased substantially and the decrement of MG-II was more than that of MG-III because toluene had a stronger interaction with Ag compared with cyclohexene through π-electrons.

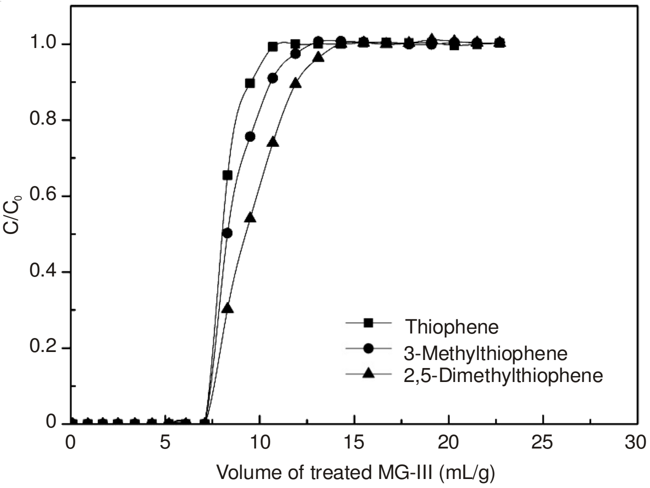

Fig. 7. Breakthrough curves of MG-III over Ag-SAC

Conclusions

- The Ag-SAC synthesized by phenolic weak acid cation exchange resin was spherical particles and the silver loaded was in elemental state according to the analytical results of XRD spectra.
- Ag-SAC showed a better adsorption performance in the fixed-bed adsorption experiments than SAC. The total saturation sulfur capacity of Ag-SAC for MG-I was 1.7 times of that of SAC, in addition, the relative selectivity increased and followed the order: 2,5-DMT> 3-MT> T.

- Compared with MG-I, Ag-SAC showed relative poor adsorptive performance for MG-II and MG-III. The presence of toluene and cyclohexene led to a significant reduction of total saturation capacity by 57 % and 33 %, respectively. The results indicated that toluene showed stronger competitive adsorption than cyclohexene through π-electrons.

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