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# Adsorption of Benzothiophene and Dibenzothiophene on Ion-Impregnated Activated Carbons and Ion-Exchanged Y Zeolites

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This work mainly involved the investigation of the adsorption of benzothiophene (BT) and dibenzothiophene (DBT) on transition-metal ion-impregnated activated carbons and ion-exchanged Y zeolites. Five kinds of transition-metal ions,  $\text{Ag}^+$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Fe}^{3+}$ , were separately loaded on activated carbons (ACs) and the Na/Y zeolites, respectively. Adsorption isotherms were measured with the static adsorption method. Textual properties of these adsorbents were measured by using ASAP 2010. Results indicated that (1) there was no adsorption of DBT on Na/Y because the aperture size of Na/Y was smaller than the molecular size of BT, (2) the equilibrium amount adsorbed of BT on  $\text{Ag}^{\text{I}}/\text{Y}$  was the highest within six ion-exchanged zeolites studied and that on  $\text{Ni}^{\text{II}}/\text{Y}$ ,  $\text{Zn}^{\text{II}}/\text{Y}$ ,  $\text{Cu}^{\text{II}}/\text{Y}$ , and  $\text{Fe}^{\text{III}}/\text{Y}$  became improved in comparison to Na/Y, (3) the equilibrium amounts adsorbed of BT and DBT on the modified ACs followed the order:  $\text{Ag}^{\text{I}}/\text{AC} > \text{Ni}^{\text{II}}/\text{AC} > \text{Cu}^{\text{II}}/\text{AC} > \text{Zn}^{\text{II}}/\text{AC} > \text{AC} > \text{Fe}^{\text{III}}/\text{AC}$ , and (4) at low BT concentrations ( $C_s < 3 \text{ mmol/L}$ ), the ion-exchanged Y zeolites had a higher adsorption capacity of BT compared to the modified ACs because of their larger surface area of micropores, while at higher BT concentrations ( $7 < C_s < 10 \text{ mmol/L}$ ), the modified ACs had a higher adsorption capacity of BT because of their much larger surface area.

## 1. Introduction

Sulfur compounds in fuels have drawn environmental concern because they are converted to  $\text{SO}_x$  during combustion, which not only results in acid rain but also poison catalysts in catalytic converters for reducing CO and  $\text{NO}_x$ .<sup>1</sup> With the increasing demand of fuels, increasing attention is paid to sulfur issues, and thus, governments worldwide have made increasingly stringent regulations to limit sulfur levels in fuels in recent years. To meet more stringent regulations and to make ultra-low sulfur fuels for fuel cell applications,<sup>1–3</sup> ultra-deep desulfurization of liquid hydrocarbon fuels has become an increasingly important subject in environment and energy studies worldwide.

Currently, the major desulfurization technology is hydrodesulfurization (HDS), which is carried out at elevated temperature and hydrogen partial pressure to convert organosulfur compounds to hydrogen sulfide ( $\text{H}_2\text{S}$ ).<sup>4</sup> The HDS process is highly efficient in removing thiols and sulfides but not for thiophenes and thiophene derivatives. Thus, after the conventional HDS process, the major sulfur compounds remaining in the transportation fuels are the refractory sulfur compounds, such as thiophenes, benzothiophene, dibenzothiophene, and their alkylated derivatives.<sup>3</sup>

To selectively remove thiophenes and thiophene derivatives, adsorption desulfurization, on the basis of ability of a solid sorbent to selectively adsorb organosulfur compounds, is considered to be an efficient and economic desulfurization technology for ultra-clean fuels.

Adsorbent is the core of adsorption technology. Therefore, many attempts have been made to develop adsorbents for desulfurization of liquid fuels<sup>1,5–12</sup> recently. The reported adsorbents include metal oxides, metal sulfides, the reduced metals, zeolite-based materials,<sup>10–12</sup> carbon materials,<sup>1,5,6</sup> activated alumina,<sup>1</sup> and carbon-based materials.<sup>8,9</sup> Among them, carbon- and zeolite-based materials showed promising application potentials.

Activated carbon (AC) is one of the most important sorbents dominating the commercial use of adsorption. As porous materials with very high surface areas and large pore volume, ACs and carbon-based materials have been studied for deep desulfurization recently. Haji used carbon aerogels (CAs) to remove DBT from liquid hydrocarbon fuels and reported that the CAs with the larger average pore size had a higher sulfur adsorption rate and higher capacity for DBT.<sup>5</sup> Song investigated different carbon materials for the desulfurization from a model diesel fuel and concluded that the surface function group, especially the oxygen-containing functional groups, affected sulfur-adsorption capacity and selectivity.<sup>6</sup> Wang and Yang used  $\text{CuCl}/\text{AC}$ ,  $\text{PdCl}_2/\text{AC}$ , and  $\text{Pd}/\text{AC}$  for desulfurization of a model jet fuel by selective adsorption of thiophenic molecules and reported that the sulfur adsorption capacity of  $\text{PdCl}_2/\text{AC}$  was

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higher than that of CuCl/AC and Pd<sup>0</sup>/AC, in agreement with molecular orbital results.<sup>7</sup>

In addition, zeolites play an enabling role in desulfurization. Zeolites that are in commercial use today are mainly the types A, X, and Y. Zeolites are used for their special adsorption properties because of their unique surface chemistries and crystalline pore structures.<sup>8</sup> Yang used Cu<sup>I</sup>/Y and Ag<sup>I</sup>/Y to adsorb sulfur compounds from commercial fuels selectively by complexation at ambient temperature and pressure and reported that the sulfur content was reduced from 430 to <0.2 ppm by weight with a sorbent capacity of 34 cm<sup>3</sup> of clean diesel produced per gram of sorbent.<sup>9</sup> Velu, Ma, and Song reported that Ce-exchanged Y zeolites exhibited excellent adsorption capacity.<sup>10</sup> Velu and Song impregnated K<sup>+</sup> on the surface of Ni<sup>II</sup>/Y and reported that K-exchanged Y-type zeolites had much higher sulfur capacity than Ni<sup>II</sup>/Y.<sup>11</sup> Laborde-Boutet compared the selectivity of thiophene/toluene competitive adsorptions onto Na<sup>I</sup>/Y and Na<sup>I</sup>/X zeolites and found that Na<sup>I</sup>/Y had higher thiophene capacity than Na<sup>I</sup>/X and Na<sup>I</sup>/Y had much higher thiophene capacity than benzene.<sup>12</sup>

The objective of this work is to investigate the adsorption of benzothiophene (BT) and dibenzothiophene (DBT) on metal ion-exchanged Y zeolites and ion-impregnated ACs. Five kinds of transition-metal ions (Ag<sup>+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, and Fe<sup>3+</sup>) were separately loaded on the ACs by the impregnation method. Five kinds of ion-exchanged Y-type zeolites separately containing Ag<sup>+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, and Fe<sup>3+</sup> were prepared by the liquid ion-exchange method. The isotherms of BT and DBT over these adsorbents were separately measured in a static adsorption system and then were compared. The influence of the metal ions and textural properties of the modified activated carbons and the ion-exchanged Y zeolites on their adsorption toward BT and DBT will be discussed and reported here.

## 2. Experimental Section

**2.1. Materials.** The adsorbates, BT (98%) and DBT (98%), were purchased from Acros Organics, Morris Plains, NJ. The activated carbon (40–60 mesh) based on coconut shell was supplied by Zhaoyang Senyuan Activated Carbon Company, China. The Na<sup>I</sup>/Y zeolite [Brunauer–Emmett–Teller (BET) surface area = 719 m<sup>2</sup>/g with a micropore diameter of 0.795 nm] was supplied by Beijing Xianfeng Chemicals, China. AgNO<sub>3</sub>, Cu(NO<sub>3</sub>)<sub>2</sub>, Ni(NO<sub>3</sub>)<sub>2</sub>, Zn(NO<sub>3</sub>)<sub>2</sub>, Fe(NO<sub>3</sub>)<sub>3</sub>, and *n*-octane were all analytical reagents.

**2.2. Adsorbent Preparation.** Ag<sup>I</sup>/AC, Cu<sup>II</sup>/AC, Ni<sup>II</sup>/AC, Zn<sup>II</sup>/AC, and Fe<sup>III</sup>/AC sorbents were prepared by impregnating ACs with corresponding metal nitrates separately. Portions (10 g) of ACs was weighed and then separately added to 0.1 M metal nitrate [AgNO<sub>3</sub>, Cu(NO<sub>3</sub>)<sub>2</sub>, Ni(NO<sub>3</sub>)<sub>2</sub>, Zn(NO<sub>3</sub>)<sub>2</sub>, or Fe(NO<sub>3</sub>)<sub>3</sub>] aqueous solution of 100 mL volume at room temperature. After 12 h, the samples were filtered and dried at 393 K for 5 h.

Ag<sup>I</sup>/Y, Cu<sup>II</sup>/Y, Ni<sup>II</sup>/Y, Zn<sup>II</sup>/Y, and Fe<sup>III</sup>/Y sorbents were prepared by conventionally proven procedures for liquid-phase ion-exchanged zeolites. Portions (10 g) of ACs was weighed and then separately added to 0.1 M metal nitrate [AgNO<sub>3</sub>, Cu(NO<sub>3</sub>)<sub>2</sub>, Ni(NO<sub>3</sub>)<sub>2</sub>, Zn(NO<sub>3</sub>)<sub>2</sub>, or Fe(NO<sub>3</sub>)<sub>3</sub>] aqueous solution of 100 mL volume at room temperature. After 12 h, the samples were filtered and dried at 393 K for 5 h.

These adsorbents will separately be used in the equilibrium isotherm experiments.

**2.3. Model Sulfur Solutions.** In the present study, two model sulfur solutions were prepared by adding sulfur compound to liquid *n*-octane. The concentrations of both BT and DBT solutions were respectively 0.01 mol/L.

**2.4. Batch Isotherm Equilibrium Studies.** Batch adsorption experiments were conducted in a temperature-controlled shaker (30°) to obtain the isotherms of BT and DBT on the zeolites and

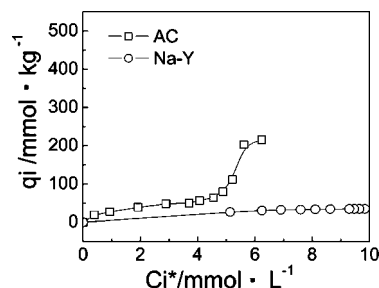


Figure 1. Isotherms of BT on AC and Na<sup>I</sup>/Y at 30°C.

ACs using the static technique.<sup>13,14</sup> A total of 0.03–1.0 g of adsorbents were separately added into a series of 10 mL test tubes each filled with 5 mL of BT or DBT solution with an initial concentration of 0.01 mol/L. The test tubes were then sealed, placed in a thermostatic shaker bath, and shaken at 100 rpm for 48 h. During the adsorption, the temperatures of the system were kept constant at 303 K.

After equilibrium, the sulfur concentrations of the treated samples were analyzed by high-performance liquid chromatography (HPLC). The chromatographic separation was achieved on an ODS-C<sub>18</sub> column at 298 K. The mobile-phase composition was 100% HPLC-grade methanol. The flow rate was 1.0 mL/min, and the eluent was monitored at 220 nm through a UV detector.

The equilibrium amount  $q_i$  of BT or DBT taken up by the adsorbents was determined on the basis of the following material balance equation:

$$q_i = \frac{V}{M_i}(C_0 - C_i^*) \quad (1)$$

where  $q_i$  is the equilibrium adsorption capacity of sulfur on the adsorbent (mg of S/g),  $C_0$  and  $C_i^*$  are the initial and equilibrium concentration of sulfur solutions (mg of S/L), respectively,  $V$  is the volume of solution (L), and  $M_i$  is the mass of the adsorbent used (g).

**2.5. Characterization of the Adsorbents. Textural Features of the Adsorbent.** The textural features (BET surface areas and pore sizes) were measured by physical adsorption of N<sub>2</sub> at 77 K using a Micromeritics ASAP2010 surface area and porosimetry analyzer. The BET surface area was calculated from adsorption isotherms using the standard BET equation. The  $t$ -plot method was applied to derive the micropore surface area.<sup>15</sup>

**Elemental Metal Content on AC Sorbents.** The loading of metal ion in the metal ion-impregnated ACs was measured by combustion experiments.<sup>7</sup> The combustion experiments were carried out for the supported sorbents (Ag<sup>I</sup>/AC, Cu<sup>II</sup>/AC, Ni<sup>II</sup>/AC, Zn<sup>II</sup>/AC, and Fe<sup>III</sup>/AC) as well as the activated carbon support and pure metal salts [AgNO<sub>3</sub>, Cu(NO<sub>3</sub>)<sub>2</sub>, Ni(NO<sub>3</sub>)<sub>2</sub>, Zn(NO<sub>3</sub>)<sub>2</sub>, or Fe(NO<sub>3</sub>)<sub>3</sub>]. The loadings of metal salts on activated carbon could then be calculated by the comparison of the “ash” contents between the sorbents, activated carbon, and pure metal salts.

**Elemental Metal Contents on Zeolite Sorbents.** The metal content in the metal ion-exchanged Y-type zeolites (Ag<sup>I</sup>/Y, Cu<sup>II</sup>/Y, Ni<sup>II</sup>/Y, Zn<sup>II</sup>/Y, and Fe<sup>III</sup>/Y) was determined using an inductively coupled plasma–atomic emission spectrometer<sup>10</sup> (ICP–AES, Spectro Ciros). The samples were dissolved in HF solution to remove zeolite framework and mixed with aqua regia to completely dissolve metal ions before analysis.

## 3. Results and Discussion

**3.1. Isotherms of BT and DBT on the Original AC and Na<sup>I</sup>/Y.** Figures 1 and 2 show separately the isotherms of BT

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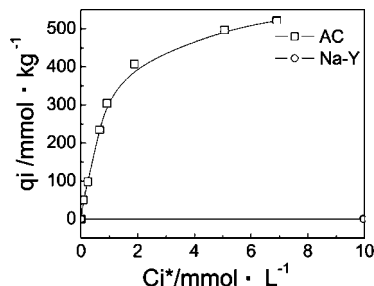


Figure 2. Isotherms of DBT on AC and Na<sup>+</sup>Y at 30°C.

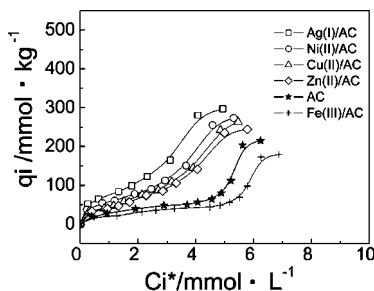


Figure 3. Isotherms of BT on ACs loaded with different metal ions at 30°C.

and DBT on AC and Na<sup>+</sup>Y. It can be seen that there is high DBT adsorptions on AC; however, no DBT adsorption occurs at all on Na<sup>+</sup>Y. That is to say that AC is able to adsorb DBT, whereas Na<sup>+</sup>Y is not. This is because the geometric factors as size and shape of both adsorbent and the adsorbed molecule play an important role for the adsorption on zeolites. With the calculation by Hyperchem 7.0, it shows that the dimension of BT and DBT are around 6.92 and 9.12 Å separately, whereas Na<sup>+</sup>Y shows a large amount of pores with a diameter of 7.952 Å characterized by ASAP2010, which are not accessible to DBT but BT molecules. In other words, the pore openings of the Na<sup>+</sup>Y are too small compared to the size of the DBT molecule, and thus, DBT cannot enter the pore system of Na<sup>+</sup>Y, which prevents DBT adsorption from occurring.

It should be noted however that BT was adsorbed on Na<sup>+</sup>Y to a negligible extent, despite its ability to enter the pore system of Na<sup>+</sup>Y. It appears that the access to the pore system of Na<sup>+</sup>Y by the thiophenic compounds is a necessary but not sufficient condition. In other words, the adsorption of the thiophenic compounds on an adsorbent not only depends upon the sizes of both adsorbent pores and adsorbate molecule but also the surface chemistry of the adsorbent. A virtual lack of BT adsorption on Na<sup>+</sup>Y is because the interaction between BT and Na<sup>+</sup>Y surfaces is weak because of Na<sup>+</sup> being too hard of an acid, whereas BT being too soft of a base, which will be further discussed later on the basis of the HSAB principle in this work.

**3.2. Effects of Different Ions on Isotherms of BT and DBT.** Figures 3 and 4 show the isotherms of BT and DBT on five different activated carbons, Ag<sup>+</sup>/AC, Ni<sup>2+</sup>/AC, Zn<sup>2+</sup>/AC, Cu<sup>2+</sup>/AC, and Fe<sup>3+</sup>/AC, at 303 K. It can be seen that the loading of different transition-metal ions on the AC surfaces resulted in the variation of BT and DBT adsorption capacities. The equilibrium amount adsorbed of BT and DBT on Ag<sup>+</sup>/AC was the highest, while that on Fe<sup>3+</sup>/AC was the lowest. The equilibrium amount adsorbed of BT and DBT on Ni<sup>2+</sup>/AC, Cu<sup>2+</sup>/AC, and Zn<sup>2+</sup>/AC became improved in comparison to the original AC.

A comparison of Figures 3 and 4 shows that the adsorption capacity of the ACs for BT is always lower than that for DBT, which is probably ascribed or related to the relative sizes of BT and DBT molecules under the condition of certain pore/

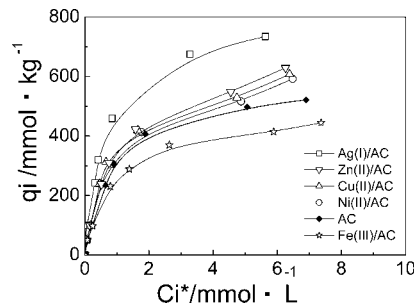


Figure 4. Isotherms of DBT on ACs loaded with different metal ions at 30°C.

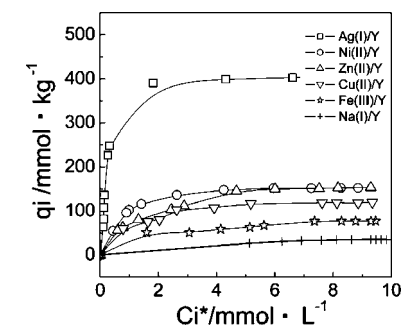


Figure 5. Isotherms of BT on various Y zeolites loaded with different metal ions at 30°C.

cavity sizes of the ACs besides surface chemistry of the ACs. When a molecule is placed between two flat surfaces, i.e., in a slit-shaped pore of activated carbon, it interacts with surfaces.<sup>8</sup> A stronger interaction with adsorbate molecules is a direct consequence of the small pore sizes. That is to say, smaller pores give rise to a stronger overlap of potentials from surrounding surfaces, and thus, there are stronger attraction forces acting on the adsorbate molecule. The ACs used in this work has certain pore/cavity structures/sizes, and thus in this case, the larger the size of a molecule within the pores, the stronger the attraction forces acting on the adsorbate molecule relative to a smaller molecule. Therefore, the pore surfaces of the ACs have stronger interactions with adsorbate DBT compared to BT because the size of DBT is larger than that of BT. As a consequence of that, the adsorption capacity for BT is always lower than that for DBT on the same AC.

In addition, it can be seen from Figures 3 and 4 that the shape of the isotherms of BT and DBT on the ACs is quite different. The isotherms of BT have a somewhat stepwise (SW) character, indicating the weak interactions/affinities between BT and the surfaces of the ACs, while the isotherms of DBT have a Langmuir (L) character, suggesting that the strong interactions/affinities between DBT and the surfaces of the ACs.

Figure 5 shows the isotherms of BT on five different zeolites, Ag<sup>+</sup>/Y, Ni<sup>2+</sup>/Y, Zn<sup>2+</sup>/Y, Cu<sup>2+</sup>/Y, and Fe<sup>3+</sup>/Y, at 303 K. It should also be noticed that the loading of different transition-metal ions on zeolite surfaces resulted in the variation of BT adsorption capacity. The equilibrium amount adsorbed of BT on Ag<sup>+</sup>/Y was the highest, while that on Na<sup>+</sup>/Y was the lowest. The equilibrium amount adsorbed of BT on Ni<sup>2+</sup>/Y, Zn<sup>2+</sup>/Y, Cu<sup>2+</sup>/Y, and Fe<sup>3+</sup>/Y became improved in comparison to Na<sup>+</sup>/Y.

Generally speaking, adsorption property of an adsorbent not only was determined by its porous microtexture but was also strongly influenced by the chemical property of its surface.<sup>15,16</sup>

Table 1 lists the content of metal elements on the ACs prepared separately by impregnation with solutions of nitrate



**Table 1. Content of the Metal Element Loaded on the ACs**

sorbent	metal ion impregnated	content of metal element loaded (mmol/g)
AC		
Ag <sup>I</sup> /AC	Ag <sup>+</sup>	0.507
Cu <sup>II</sup> /AC	Cu <sup>2+</sup>	0.491
Ni <sup>II</sup> /AC	Ni <sup>2+</sup>	0.479
Zn <sup>II</sup> /AC	Zn <sup>2+</sup>	0.488
Fe <sup>III</sup> /AC	Fe <sup>3+</sup>	0.495

**Table 2. Contents of Metal Elements and H<sup>+</sup> on Y-Zeolite Sorbents**

ion exchanged zeolites	metal ion exchanged	content of exchanged metal element (mmol/g)	content of residual Na <sup>+</sup> ion (mmol/g)	content of exchanged H <sup>+</sup> (mmol/g)
Ag <sup>I</sup> /Y	Ag <sup>+</sup>	0.75 for Ag <sup>I</sup>	1.09	$1.64 \times 10^{-4}$
Cu <sup>II</sup> /Y	Cu <sup>2+</sup>	0.74 for Cu <sup>II</sup>	1.74	$2.02 \times 10^{-3}$
Ni <sup>II</sup> /Y	Ni <sup>2+</sup>	0.73 for Ni <sup>II</sup>	1.83	$2.00 \times 10^{-5}$
Zn <sup>II</sup> /Y	Zn <sup>2+</sup>	0.73 for Zn <sup>II</sup>	1.39	$6.40 \times 10^{-5}$
Fe <sup>III</sup> /Y	Fe <sup>3+</sup>	0.95 for Fe <sup>III</sup>	1.17	0.0188

salts. It can be seen that the metal element Ag<sup>+</sup>, Cu<sup>2+</sup>, Ni<sup>2+</sup>, Zn<sup>2+</sup>, or Fe<sup>3+</sup> had been loaded onto the surfaces of the ACs, and each of the ACs has a close content value for the corresponding element component.

Table 2 lists the content of exchanged elements on the Y-type zeolites. It indicates that each of the ion-exchanged zeolites, except Fe<sup>III</sup>/Y, has a close concentration value for the corresponding element component, Ag<sup>+</sup>, Cu<sup>2+</sup>, Ni<sup>2+</sup>, or Zn<sup>2+</sup>. Meanwhile, it was also noticed that there might be the occurrence of hydrolysis phenomena of metal ions and H<sup>+</sup> ions could be exchanged with Na<sup>+</sup>/Y zeolite. In our experiments, it was found that solution pH values rose somewhat after these nitrate salt solutions were separately used for impregnation of zeolites, indicating that the H<sup>+</sup> ion concentration of the solutions decreased because the H<sup>+</sup> ions had partly been exchanged into zeolite. For example, the initial pH values of various nitrate salt solutions, which separately contained AgNO<sub>3</sub>, Cu(NO<sub>3</sub>)<sub>2</sub>, Ni(NO<sub>3</sub>)<sub>2</sub>, Zn(NO<sub>3</sub>)<sub>2</sub>, and Fe(NO<sub>3</sub>)<sub>3</sub>, were respectively 4.44, 3.52, 5.81, 5.23, and 2.38, and then their final pH values became 4.46, 3.55, 5.87, 5.28, and 2.40 because of the exchange of part H<sup>+</sup> ions with the Na<sup>+</sup>/Y. The amounts exchanged of H<sup>+</sup> on the zeolites were calculated on the basis of the mass balance principle and also listed in Table 2. However, it was found that the contents of exchanged H<sup>+</sup> in the Y-type zeolites were very low compared to other metal ion, such as Ag<sup>+</sup>, Cu<sup>2+</sup>, Ni<sup>2+</sup>, Zn<sup>2+</sup>, or Fe<sup>3+</sup>, as indicated in Table 2.

In this work, the HSAB principle, which was proposed by Pearson,<sup>17</sup> will be used to explain the effects of the local hardness of the AC and zeolite surfaces on its adsorption of BT and DBT. The HSAB principle was locally applied: "hard regions of a system prefer to interact with hard reagents whereas soft regions prefer soft species".<sup>18</sup> To make a quantitative calculation of the hardness, the density functional theory (DFT) was applied by Parr and Pearson.<sup>19</sup> The absolute hardness and electronegativity of BT can be estimated using the following formula<sup>19–21</sup> from DFT for its soft/hard property:

$$\eta = 1/2(I - A) \quad (2)$$

where  $\eta$ , the absolute hardness (always positive), is half the difference between  $I$ , the ionization energy, and  $A$ , the electron affinity.  $I$  and  $A$  can be found using the following equations:

$$I = -E_{\text{HOMO}} \quad (3)$$

$$A = -E_{\text{LUMO}} \quad (4)$$

**Table 3.  $E_{\text{LUMO}}$ ,  $E_{\text{HOMO}}$ , Hardness, and Electronegativity Value for BT (eV)**

molecule	$E_{\text{HOMO}}$	$E_{\text{LUMO}}$	$\eta$	$\chi$
BT	-8.240	2.963	5.602	2.638
DBT	-7.939	2.594	5.267	2.673

**Table 4. Pearson Classification and Absolute Hardness of Metal Ions<sup>19</sup>**

Pearson classification	soft acid	borderline acid				hard acid		
metal ions	Ag <sup>+</sup>	Cu <sup>2+</sup>	Ni <sup>2+</sup>	Zn <sup>2+</sup>	Fe <sup>3+</sup>	Na <sup>+</sup>	H <sup>+</sup>	
absolute hardness, $\eta$	6.9	8.3	8.5	10.8	13.1	21.1	+	∞

where  $E_{\text{LUMO}}$  is the lowest unoccupied molecular orbital (LUMO) energy and  $E_{\text{HOMO}}$  the highest occupied molecular orbital (HOMO) energy.

Inserting eqs 3 and 4 into eq 2, one can obtain

$$\eta = 1/2(E_{\text{HOMO}} - E_{\text{LUMO}}) \quad (5)$$

and thus electronegativity  $\chi$  can be found by the following equation:

$$\chi = 1/2(I + A) = -1/2(E_{\text{HOMO}} + E_{\text{LUMO}}) \quad (6)$$

In this work, *ab initio* MO calculations for BT were performed. The basis set was 3-21G, and Hyperchem 7.0 program systems were used to calculate the charge distribution,  $E_{\text{LUMO}}$  and  $E_{\text{HOMO}}$ , of the BT molecules. Then, the hardness value and electronegativity of BT were separately calculated on the basis of eqs 2 and 6. The absolute hardness  $\eta$  of BT was 5.602, and its electronegativity was 2.638. In the same way, the absolute hardness  $\eta$  of DBT was 5.267, and its electronegativity was 2.673, which were listed in Table 1. In terms of Pearson hard–soft base classification, BT and DBT were considered as soft bases because of their absolute electronegativity < 2.8.<sup>17,19,20</sup> The computer results were listed in Table 3.

On the other hand, the transition-metal ions were taken for Lewis acid.<sup>22</sup> According to Pearson classification, the ion Ag<sup>+</sup> belonged to soft acid, the ions Cu<sup>2+</sup>, Ni<sup>2+</sup>, and Zn<sup>2+</sup> belonged to borderline acids, and the ions Fe<sup>3+</sup> and Na<sup>+</sup> belonged to hard acid.<sup>19,24</sup> The absolute hardness of these metal ions is listed in Table 4. When these different metal ions were separately loaded onto the adsorbents, the surface local hardness of the adsorbents could be changed.

For the modified ACs prepared by the impregnation method, according to the HSAB principle that hard acids prefer to bond to hard bases and soft acids prefer to bond to soft bases,<sup>17,19,20,22</sup> it can be predicted that the loading of Ag<sup>+</sup> could enhance the interaction between BT and Ag<sup>I</sup>/AC surfaces or DBT and Ag<sup>I</sup>/AC surfaces because Ag<sup>+</sup> was a soft acid and BT and DBT were both soft bases. In addition, it can also be predicted that the loading of Fe<sup>3+</sup> will most likely weaken the interaction between BT and Fe<sup>III</sup>/AC surfaces or DBT and Fe<sup>III</sup>/AC surfaces because Fe<sup>3+</sup> was a hard acid, while BT and DBT were both soft bases. It should be noticed that the HSAB principle could not be used to predict the interaction between the soft base and the borderline acids. However, the results of the equilibrium isotherms of BT and DBT had indicated that the equilibrium

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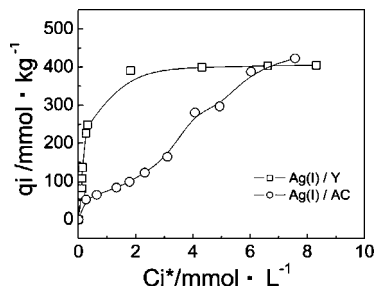


Figure 6. Isotherms of BT on both Ag<sup>I</sup>/Y and Ag<sup>I</sup>/AC at 30°C.

amount adsorbed of BT and DBT on Ni<sup>II</sup>/AC, Cu<sup>II</sup>/AC, and Zn<sup>II</sup>/AC became improved in comparison to the original AC, as shown in Figures 3 and 4, suggesting the loading of these borderline acid ions could enhance the interaction between BT/DBT and the resulting AC surfaces. The reasons may be that, because the ions Ni<sup>2+</sup>, Cu<sup>2+</sup>, and Zn<sup>2+</sup> were the borderline acids, the loading of ion Ni<sup>2+</sup>, Cu<sup>2+</sup>, or Zn<sup>2+</sup> on the surfaces of the activated carbon could weaken the local hard acids of the surfaces, so that adsorption of BT/DBT was enhanced to some extent.

Similarly, for the various ion-exchanged zeolites, it can also be predicted on the basis of the HSAB principle that, if Na<sup>I</sup>/Y zeolite was exchanged with Ag<sup>+</sup>, it would enhance the interaction between BT and the resulting Ag<sup>I</sup>/Y zeolite because Ag<sup>+</sup> was a soft acid and BT was a soft base. Although the HSAB principle could not be used to predict the interaction between the soft base and the borderline acids, it was found that, after Na<sup>I</sup>/Y zeolite was exchanged with borderline acid ion Zn<sup>2+</sup>, Ni<sup>2+</sup>, or Cu<sup>2+</sup>, the equilibrium amounts adsorbed of BT on the resulting ion-exchanged zeolites were increased in comparison to Na<sup>I</sup>/Y zeolite, as shown in Figure 5. The reason may be that, when ion Na<sup>+</sup> of Na<sup>I</sup>/Y zeolite was exchanged separately with ion Zn<sup>2+</sup>, Ni<sup>2+</sup>, or Cu<sup>2+</sup>, it could weaken the local hard acids of the Y-zeolite surfaces, so that adsorptions of BT were enhanced to some extent. Although both Na<sup>+</sup> and Fe<sup>3+</sup> were hard acids, it was found that, after Na<sup>I</sup>/Y zeolite was exchanged with Fe<sup>3+</sup>, the equilibrium amount of BT on the resulting Fe<sup>III</sup>/Y zeolite was increased somewhat, which may be due to hardness of Na<sup>+</sup> being harder than that of Fe<sup>3+</sup>, as indicated in Table 4.

In addition, it should be mentioned that the H<sup>+</sup> ions of the solutions were partly exchanged into zeolite because of the occurrence of the hydrolysis phenomena of metal ions and thus the production of H<sup>+</sup> ions in ion-exchange processes. However, the amount of exchanged H<sup>+</sup> onto the Y-type zeolites was very low in comparison to the other exchanged metal ions, as indicated in Table 2. On the other hand, H<sup>+</sup> is usually considered as a hard acid, and its hardness is nearly infinite as shown in Table 4. Therefore, it can be deduced on the basis of the HSAB principle that the contribution of the ion H<sup>+</sup> to the BT-ion-exchanged zeolites interaction would be extremely weak or small because not only is it a hard acid but its hardness is also much higher than Fe<sup>3+</sup> and Na<sup>+</sup>. As a consequence of that, its influence on the adsorption of BT on the ion-exchanged zeolites is very weak and negligible.

**3.3. Comparisons of BT Isotherms on Ion-Impregnated ACs and Ion-Exchanged Y Zeolites.** Figures 6–10 show the comparison of isotherms of BT on both the modified ACs and the various ion-exchanged Y zeolites. It was found that, at lower BT concentrations ( $C_s < 3$  mmol/L), the equilibrium amounts adsorbed of BT on the ion-exchanged Y zeolites Ag<sup>I</sup>/Y, Ni<sup>II</sup>/Y, Zn<sup>II</sup>/Y, Cu<sup>II</sup>/Y, and Fe<sup>III</sup>/Y were higher than those on the corresponding modified ACs. On the other hand, at higher BT concentrations ( $7 < C_s < 10$  mmol/L), the equilibrium amounts

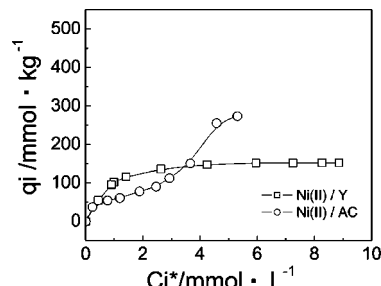


Figure 7. Isotherms of BT on both Ni<sup>II</sup>/Y and Ni<sup>II</sup>/AC at 30°C.

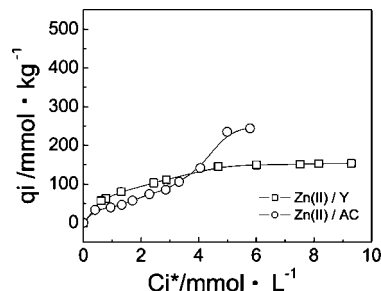


Figure 8. Isotherms of BT on both Zn<sup>II</sup>/Y and Zn<sup>II</sup>/AC at 30°C.

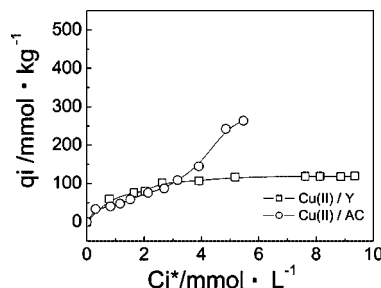


Figure 9. Isotherms of BT on both Cu<sup>II</sup>/Y and Cu<sup>II</sup>/AC at 30°C.

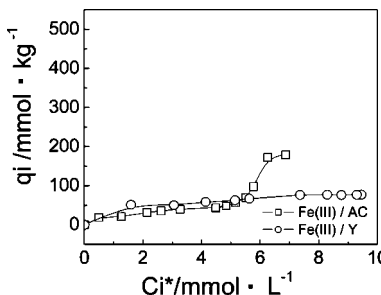


Figure 10. Isotherms of BT on both Fe<sup>III</sup>/Y and Fe<sup>III</sup>/AC at 30°C.

Table 5. Textural Features of the Modified ACs and Ion-Exchanged Y Zeolites

adsorbent	Ag <sup>I</sup> /AC	Ni <sup>II</sup> /AC	Zn <sup>II</sup> /AC	Cu <sup>II</sup> /AC	Fe <sup>III</sup> /AC
BET surface area (cm <sup>2</sup> /g)	1036	1145	1001	1110	1077
micropore area (cm <sup>2</sup> /g)	522	547	509	516	558
adsorbent	Ag <sup>I</sup> /Y	Ni <sup>II</sup> /Y	Zn <sup>II</sup> /Y	Cu <sup>II</sup> /Y	Fe <sup>III</sup> /Y
BET surface area (cm <sup>2</sup> /g)	693	714	639	681	684
micropore area (cm <sup>2</sup> /g)	647	651	599	633	652

adsorbed of BT on these ion-exchanged Y zeolites were lower than those on the corresponding modified ACs. This mainly ascribed to the textural properties of these adsorbents.

Table 5 lists the textural features of the modified ACs and ion-exchanged Y zeolites. The data in Table 5 indicated that, although the surface area of the ion-exchanged Y zeolites was much smaller than those of the modified ACs, their micropore surface area was larger in comparison to the modified ACs. Generally speaking, at low BT concentrations, the adsorption

of micropores for BT was dominant,<sup>25</sup> and the more the micropores of adsorbent, the higher its adsorption capacity for BT. As a consequence, the adsorption capacity of the ion-exchanged Y zeolites for BT was higher than those of the modified ACs because the micropore surface area of the former was higher than those of the latter. The higher the micropore surface area of the adsorbent, the higher its BT adsorption capacity. When the concentration of adsorbates increased, adsorption occurred in meso- and micropores.<sup>26</sup> Thus, at higher BT concentrations, the mesopore of the modified ACs would gradually play a role in adsorption of BT after all of the micropores were occupied. The amounts adsorbed of BT were dependent upon the micropores of the adsorbents but also the total surface area and pore volume of the adsorbents.<sup>25,27</sup> Because the modified ACs had higher surface area and pore volume than the ion-exchanged Y zeolites, their adsorption capacity of BT was higher than the ion-exchanged Y zeolites, at higher BT concentrations ( $7 < C_s < 10$  mmol/L), as shown in Figures 6–10.

#### 4. Conclusion

From the foregoing discussion, the following conclusions can be drawn: (1) There was no adsorption of DBT on Na<sup>I</sup>/Y zeolite because the aperture size of the Na<sup>I</sup>/Y zeolite was smaller than the molecular size of BT, and thus, DBT remained excluded. The virtual lack of BT adsorption on Na<sup>I</sup>/Y was because of BT being a soft base and Na<sup>+</sup> a strong acid; therefore, the interaction

between BT or DBT and Na<sup>I</sup>/Y surfaces is weak. (2) The loading of different transition-metal ions on the carbon surfaces resulted in the variation of BT and DBT adsorption capacities. The equilibrium amount adsorbed of BT and DBT on Ag<sup>I</sup>/AC was the highest, while that on Fe<sup>III</sup>/AC was the lowest. The equilibrium amount adsorbed of BT on Ni<sup>II</sup>/AC, Cu<sup>II</sup>/AC, and Zn<sup>II</sup>/AC became improved in comparison to the original AC. (3) The amount adsorbed of BT on the Ag<sup>I</sup>/Y was the highest, while that on the Na<sup>I</sup>/Y was the lowest within six ion-exchanged zeolites studied. The amount adsorbed of BT on Ni<sup>II</sup>/Y, Zn<sup>II</sup>/Y, Cu<sup>II</sup>/Y, and Fe<sup>III</sup>/Y became improved in comparison to the Na<sup>I</sup>/Y. (4) At low BT concentrations ( $C_s < 3$  mmol/L), the ion-exchanged Y zeolites had a higher adsorption capacity of BT compared to the correspondingly modified ACs because these ion-exchanged Y zeolites had more surface area of micropores and the adsorption BT was mainly dependent upon micropore adsorption of the adsorbent at low concentration. (5) At higher BT concentrations ( $7 < C_s < 10$  mmol/L), the modified ACs had higher adsorption capacity of BT compared to the correspondingly ion-exchanged Y zeolites because the modified ACs had a larger surface area than these ion-exchanged Y zeolites.

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**Supporting Information Available:** Adsorption dynamics and concentration of H<sup>+</sup> on modified zeolites. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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