



# Density functional theory study of adsorption of benzothiophene and naphthalene on silica gel



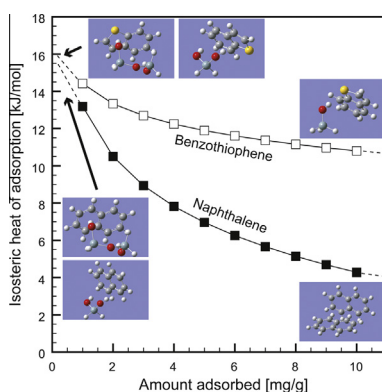
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## HIGHLIGHTS

- The mechanisms of benzothiophene and naphthalene adsorption on silica surface were investigated.
- The isolated and geminal silanols might interact with benzothiophene selectively.
- The vicinal silanols might interact with naphthalene selectively.
- Multilayer adsorption might occur for both adsorbates through T-shape interactions.

## GRAPHICAL ABSTRACT



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## ABSTRACT

The adsorptive removal of sulfur-containing compounds such as thiophene and dibenzothiophene derivatives from transportation fuels has received extensive attention because of the economical and environmental advantages of adsorptive removal compared to the hydrodesulfurization process. Metal-ion-exchanged zeolites have been known to exhibit high desulfurization performance. However, zeolites induce side reactions because of their strong acidity. Accordingly, silica-based adsorbents showing lower acidity have potential for the desulfurization adsorbent. In this study, to facilitate the development of efficient desulfurization adsorbents, the mechanisms of benzothiophene and naphthalene adsorption onto silica surface were investigated using density functional theory (DFT) in conjunction with experimental approaches. Both the computational and the experimental results suggested that the sites at which benzothiophene and naphthalene adsorb onto silica gel are different types of silanol groups. The adsorption sites of benzothiophene at the initial stage were vicinal-type and/or geminal-type silanols and the final adsorption sites were isolated-type silanols. In addition, the results of DFT calculations suggest that multilayer adsorption might occur. In contrast, the adsorption sites of naphthalene at the initial stage were vicinal-type silanols. Afterward, multilayer adsorption through a T-shape interaction might occur successively on the silica surface.

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## 1. Introduction

The presence of sulfur-containing compounds in transportation fuels is one of the major causes of air pollution. Furthermore, they lead to the deterioration of combustion engines. Numerous countries have recently regulated the sulfur levels in fuels. In Japan,

### Nomenclature

$c_e$	the equilibrium concentration at temperature $T$	$m$	weight of adsorbent
$c_{i,e}$	equilibrium concentrations of component $i$	$n$	Freundlich coefficients
$c_{i,0}$	initial concentrations of component $i$	$q_e$	equilibrium amount adsorbed
$E_{\text{adsorbate}}$	total energy of adsorbent	$q_{i,e}$	equilibrium amount of component $i$ adsorbed
$E_{\text{adsorbent}}$	total energy of adsorbent	$q_{st}$	isosteric heat of adsorption (absolute value of $\Delta H_{ad}$ )
$E_{\text{interaction}}$	total energy of interaction state	$R$	gas constant
$\Delta E_{ad}$	interaction energy	$T$	adsorption temperature
$\Delta H_{ad}$	differential enthalpy of adsorption	$V$	solution volume
$k$	Freundlich coefficients		

the sulfur content in gasoline and diesel fuel has been limited to 10 ppm since 2008. Similar regulations also have been implemented in the US and in the EU since 2006 and 2009, respectively. Furthermore, kerosene has been investigated as a hydrogen source for domestic-use fuel cells. However, the sulfur content in kerosene causes steam-reforming and fuel-cell catalyst degradations.

Accordingly, desulfurization of fuels has been a topic of intensive research over the past several decades. Although almost all sulfur compounds can be removed from petroleum feedstock by the hydrodesulfurization process, this process is less effective for aromatic thiophenes and thiophene derivatives [1–3]. According to the literature [4,5], the main remaining sulfur compounds in FCC gasoline are thiophene, benzothiophene, and their alkylated derivatives. In the case of diesel, the remaining compounds are dibenzothiophene and its alkylated derivatives.

To remove these compounds, numerous desulfurization methods have been proposed and used in actual processes, including catalytic hydrodesulfurization and adsorptive desulfurization [2,5–18]. Novel catalysts have been developed for hydrodesulfurization, and some of these catalysts enable the removal aromatic thiophenes and thiophene derivatives [5–7,19–21]. However, several methods are used sequentially in actual desulfurization processes for decreasing sulfur levels. Furthermore, hydrodesulfurization is expensive and consumes a large amount of energy because it is performed at high temperatures and pressures. In contrast, adsorption has economical and environmental advantages for the removal of sulfur compounds because it can be performed under ambient temperature and pressure. However, the selective removal of thiophene derivatives is difficult because of the coexistence of structurally similar aromatic compounds. Therefore, the improvement of adsorbent performance and/or the development of novel adsorbents are desired to further enhance desulfurization.

To date, many attempts on adsorptive desulfurization have been conducted. Metal-ion-exchanged zeolites exhibit high desulfurization performance [2,9,16,22–24]; however, zeolites cause side reactions because of their strong acidity. To avoid undesirable reactions, less-reactive adsorbents are needed. Silica-based adsorbents, including silica gel with lower acidity, are considered potential adsorbents for deep desulfurization. According to spectroscopy studies of the adsorption of thiophenic compounds onto silica materials, the silanol groups are the main interaction sites [25–27]. However, few studies have quantitatively assessed this interaction.

In the removal of thiophenic compounds by adsorption, structurally similar aromatic compounds interfere with the adsorption of thiophenes. In this study, achieving a better understanding of the mechanisms of benzothiophene and naphthalene adsorption onto silica was focused to design an efficient desulfurization adsorbent. Adsorption sites and states were estimated from heats of adsorption obtained by both experimental and computational approaches.

## 2. Material and methods

### 2.1. Materials

The adsorbent used in this study was silica gel CARIACT Q-6 manufactured by Fuji Silysia Chemical, Ltd. (Japan). The silica gel was dried at 393 K for 24 h in a vacuum oven before being used in experiments. The physical properties of the CARIACT Q-6 are listed in Table 1.

The adsorbates used in this study were benzothiophene and naphthalene, which were obtained from Junsei Chemical Co., Ltd. (Japan) and Tokyo Chemical Industry Co., Ltd. (Japan), respectively. Isooctane (2,2,4-trimethylpentane) obtained from Junsei Chemical Co., Ltd. (Japan) was used as a model fuel. All chemicals were used without further purification.

### 2.2. Adsorption experiments

The equilibrium adsorption isotherms for single-component and binary-component systems were determined using the conventional batch bottle technique. The contact time was 2 days in a constant-temperature bath at 5 °C, 15 °C, or 25 °C. The equilibrium concentrations of each component were measured using a GC-18A (Shimadzu Co., Japan) gas chromatograph equipped with TC-17 capillary column (GL Sciences Inc., Japan) and a flame ionization detector. The amount adsorbed was calculated using the following equation:

$$q_{i,e} = (c_{i,0} - c_{i,e}) \frac{V}{m} \quad (1)$$

In this equation,  $q_{i,e}$  is the equilibrium amount of component  $i$  adsorbed;  $c_{i,0}$  and  $c_{i,e}$  are the initial and equilibrium concentrations of component  $i$ , respectively;  $m$  is the weight of adsorbent; and  $V$  is solution volume.

As shown in a later section, experimentally obtained adsorption isotherms of both adsorbates followed the Freundlich-type isotherm model (Eq. (2)),

$$q_{i,e} = k c_{i,e}^{1/n} \quad (2)$$

where  $k$  and  $n$  are Freundlich coefficients.

**Table 1**  
Properties of CARIACT Q-6 silica.

Property	Value
Specific surface area (m <sup>2</sup> /g)	430
Pore volume (cm <sup>3</sup> /g)	0.61
Packing density (g/cm <sup>3</sup> )	0.62
Average pore size (nm)	6
Particle size (mm)	0.85–1.70

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