

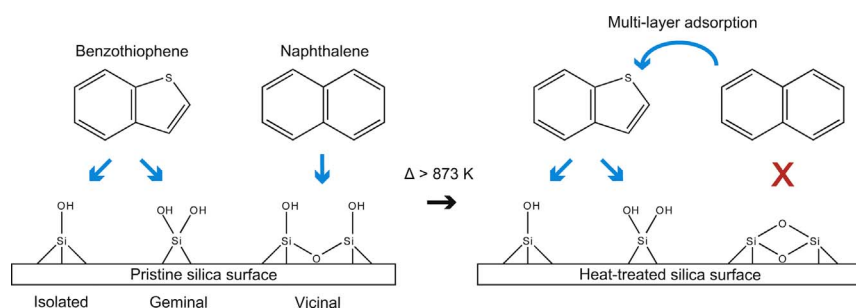


Full Length Article

Role of silanol groups on silica gel on adsorption of benzothiophene and naphthalene

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GRAPHICAL ABSTRACT



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ABSTRACT

The adsorptive removal of sulfur-containing compounds such as thiophene derivatives from transportation fuels has received extensive attention because of its economic and environmental advantages compared to the hydrodesulfurization process. In our previous study, we suggested that the adsorption sites for benzothiophene and naphthalene on the silica surface consist of different types of silanol groups, and the removal of vicinal silanols from the silica surface should enable silica materials to adsorb benzothiophene selectively. In this study, an attempt is made to prove this hypothesis for the development of novel desulfurization sorbents. Heat treatment of silica gel was performed at different temperatures to remove vicinal silanol groups, and the adsorption capacities of benzothiophene and naphthalene were evaluated. The amount of naphthalene adsorbed on heat-treated silica gel decreased with increasing heat-treatment temperature, whereas the amount of benzothiophene adsorbed on silica gel treated at 873 and 1073 K showed only a slight decrease. Considering the heat treatment might lead to the removal of vicinal silanols due to dehydration of surface silanols, the results indicate that vicinal silanol groups were selective adsorption sites for naphthalene. Moreover, for binary-component systems, the adsorption capacities of benzothiophene and naphthalene were almost identical because of multilayer adsorption of naphthalene on adsorbed benzothiophene, and the adsorption capacities of benzothiophene for single- and binary-component systems were also identical. This suggests that the heat treatment of silica enables the selective removal of benzothiophene.

1. Introduction

Sulfur-containing compounds in transportation fuels are one of the

major causes of air pollution, and lead to combustion engine deterioration. Many countries have issued regulations to limit sulfur levels in fuels. For instance, in Japan, the sulfur content in gasoline and diesel

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fuel has been limited to 10 ppm since 2008. Similar regulations have been implemented in the United States and in the European Union in 2006 and 2009, respectively. In addition, kerosene has been investigated as a hydrogen source for home-use fuel cells; however, deep desulfurization of kerosene is required because sulfur-containing compounds cause degradation of steam-reforming catalysts.

Thus, the development of desulfurization techniques has become one of the most intensive research topics over the past decades. Although almost all sulfur compounds can be removed from petroleum feedstock by hydrodesulfurization, aromatic thiophenes and thiophene derivatives remain in the product [1–3]. According to the literatures [4,5], the major sulfur compounds in fluid catalytic cracking gasoline and diesel are thiophenes and benzothiophenes, and dibenzothiophenes and its alkylated derivatives, respectively.

For removal of these sulfur compounds, various desulfurization methods, such as catalytic hydrodesulfurization and adsorptive desulfurization, have been proposed and applied to real processes [6–10]. Although novel hydrodesulfurization catalysts have been developed, which enable efficient removal of aromatic thiophenes [5,6,11–13], hydrodesulfurization is an expensive and energy-consuming process because of its high-temperature and high-pressure operation. In contrast, adsorption techniques for the removal of sulfur compounds have economic and environmental advantages because they can be performed at ambient temperature and pressure.

To date, numerous studies on adsorptive desulfurization have been conducted, and it was found that ion-exchanged zeolites show high desulfurization performance [2,14–17]. However, zeolites cause side reactions due to their strong acidity. Thus, improvement of adsorption performance and/or the development of novel adsorbents are required for deep desulfurization; in particular, less reactive adsorbents are needed. For this reason, silica-based adsorbents have been explored for adsorptive desulfurization [18–21].

Aromatic compounds with similar structure interfere with the adsorptive removal of thiophenic compounds. In our previous study on the use of porous silica materials as desulfurization sorbents, the mechanism of benzothiophene and naphthalene adsorption on silica surface was investigated using density functional theory in conjunction with experimental approaches [22]. As a result, both computational and experimental results indicated that benzothiophene and naphthalene adsorption sites on the silica gel surface consist of different types of silanol groups. At the initial stage, the adsorption sites of benzothiophene are vicinal and/or geminal silanols, whereas the final adsorption sites are isolated silanols. In contrast, the naphthalene adsorption sites at the initial stage are vicinal silanols. These results suggested that the elimination of vicinal-type silanol groups from the silica surface should enable silica materials to adsorb benzothiophene selectively.

In this study, the selective modification of the silica surface to reduce the number of vicinal silanols was investigated to further validate our previous hypothesis and for the development of novel desulfurization sorbents.

2. Material and methods

2.1. Materials

Benzothiophene and naphthalene adsorbates 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.

The adsorbent used in this study was silica gel CARiACT Q-6 manufactured by Fuji Silysia Chemical, Ltd. (Japan), which was dried at 393 K for 24 h in a vacuum oven before use.

2.2. Preparation and characterization of heat-treated silica gel

Heat-treated silica gel was prepared using an electric muffle furnace. The heat treatment was performed at a target temperature (873, 1073, and 1273 K) for 24 h in air. Thus-obtained silica gels were denoted as Q-6(*T*), where *T* represents the calcination temperature.

The prepared samples were characterized by N₂ adsorption-desorption at 77 K using an ASAP 2420 (Micromeritics, Norcross, GA) automated system. The specific surface area (*S*_{BET}) and the pore size distribution were calculated by the Brunauer-Emmett-Teller (BET) and the Barrett-Joyner-Halenda (BJH) methods, respectively. The total pore volume was calculated from the amount of adsorbed N₂ at *P*/*P*₀ = 0.99. The infrared (IR) spectra of silica gel before and after heat treatment were measured on a FT/IR-4100 spectrometer (JASCO Co., Japan) by the KBr method.

2.3. Adsorption experiments

The equilibrium adsorption isotherms for single- and binary-component systems were determined using the conventional batch bottle technique. A series of known concentration solutions (25 mL) were prepared, and 1 g of adsorbent was added into each solution. The contact time was 2 days in a constant-temperature bath at 288 K. The equilibrium concentration of each component was determined using a GC-18A gas chromatograph (Shimadzu Co., Japan) equipped with a TC-17 capillary column (GL Sciences Inc., Japan) and a flame ionization detector. The adsorbed amount was calculated using the following equation:

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

where, *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 the solution volume.

3. Results and discussion

The textual structure of the prepared silica samples was characterized by N₂ adsorption-desorption isotherms at 77 K, and the results are shown in Fig. 1. N₂ adsorption isotherms of all samples showed typical type IV behavior, indicating their mesoporous nature. However, Q-6(1273) showed quite low amount of N₂ adsorbed compared to other samples, characteristic of almost non-porous materials. The physical properties of the silica materials are summarized in Table 1. Clearly, pore volume and surface area of the silica sorbent decreased with

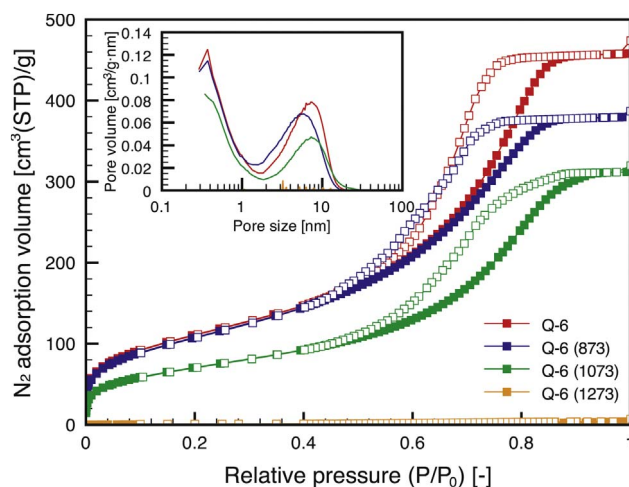


Fig. 1. N₂ adsorption-desorption isotherms and pore size distributions of the prepared silica samples.

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