

## [Research Note]

# Adsorptive Separation of Infinitesimal Sulfur Oxide in Naphtha —Screening of Adsorbents—

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A model naphtha and benzothiophene-1,1-oxide (BTDO) were used to evaluate five commercial adsorbents in order to select a high-performance adsorbent for the separation of sulfur oxides generated in oxidative desulfurization processes.

In preliminary experimental runs, the adsorbents were examined to determine their ability to reduce the sulfur concentration in the feed from 14 ppm to 1 ppm using 0.2 wt% adsorbent. Three of the five adsorbents, silica gel (SIL), active carbon-impregnated silica gel (ACSIL), and molecular sieve 13X (MS) met this criterion, while active carbon (AC) and silica-alumina type (NBD) adsorbents did not. Screening of the three adsorbents that passed the preliminary test showed that SIL had the highest throughput, which exceeded 1000 g/g-adsorbent, in reducing the sulfur concentration in model naphtha from 1 ppm to 10 ppb. ACSIL and MS could cope with only about 600 g/g-adsorbent.

**Keywords**

Oxidative desulfurization, Adsorption, Separation, Naphtha, Silica gel

**1. Introduction**

Many of the environmental problems posed by conventional vehicles should be reduced when the use of fuel cells becomes widespread<sup>1)</sup>. However, one of the more important, unresolved issues facing fuel cell technology is ensuring a constant supply of hydrogen. Liquid fuels, including gasoline, have clear advantages: the infrastructure of conventional gas stations can be used for on-site or on-board conversion, conversion efficiencies are higher, and hydrogen can be produced at a lower cost than the equivalent quantity of methanol. However, sulfur must be eliminated from any proposed liquid fuel and numerous studies have examined the issues involved.

In the solid oxide and polymer electrolyte fuel cells currently under consideration for vehicles, the sulfur content must not exceed several tens of parts per billion. Conventional hydrogenation desulfurization (HDS) results in sulfur levels of about 1 ppm<sup>2)</sup> and advanced HDS systems are being investigated to achieve the lower sulfur concentrations necessary. These include using materials that can adsorb and eliminate hydrogen sulfide during HDS<sup>3)</sup>. To date, however, no advanced HDS system has reduced sulfur levels below

20 ppb.

In the past decade, proposed alternatives to HDS include adsorption<sup>4),5)</sup> and oxidative desulfurization (ODS)<sup>6)~8)</sup>. Much of the effort has been directed at ultra-deep desulfurization of gas oils, but some studies have also examined naphthas. ODS should eventually prove effective at reducing sulfur compounds, using relatively low temperatures, under atmospheric pressure. By using a combination of oxidation with post-oxidation treatments, such as adsorption or extraction, concentrations of 20 ppb or lower appear possible<sup>9)~11)</sup>, using far less stringent conditions than those required for HDS. When the feedstock used for ODS already has a low sulfur content, sulfur-free fuels can be produced with minimal losses.

In this study, we applied ODS treatment to a hydro-treated naphtha that contained low concentrations of aromatic compounds (<1 wt%), no olefins, and 10 ppm sulfur. The oxidation process should reduce the initial sulfur concentration to about 1 ppm. When followed by adsorption separation, the remaining sulfur oxide should be reduced to 10 ppb to yield an extra-low-sulfur naphtha ("Hyper-Clean Naphtha").

Yazu *et al.*<sup>12)</sup> found that benzothiophene is the least active sulfur compound in naphtha and that its oxidation products tend to persist in naphtha after ODS. Our study was targeted specifically at establishing the optimum post-ODS treatments necessary to adsorb and

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Table 1 Properties of Adsorbent

Adsorbent	Abbreviation	Particle size [ $\mu\text{m}$ ]	Specific surface area [ $\text{m}^2/\text{g}$ ]	Activation temperature [ $^{\circ}\text{C}$ ]
Silica gel	SIL	75-150	624	130
Active carbon impregnated silica gel	ACSIL	150-180	557	130
Active carbon	AC	150-180	1150	130
Silica-alumina	NBD	75-150	320	300
Molecular sieve 13X	MS	150-180	435	300

Activation: Dried at the prescribed temperature and under 50 ml/m nitrogen stream overnight.

eliminate any oxidized benzothiophene.

## 2. Materials and Experiment

### 2.1. Reagents and Adsorbents

We used benzothiophene-1,1-dioxide (BTDO,  $\text{C}_8\text{H}_6\text{SO}_2$ ; formula weight, 166.1; Sigma Aldrich Japan) as a sulfur oxide standard, *n*-hexane and ethanol (HPLC grade; Wako Pure Chemical Industries) as eluents for HPLC analysis, and *n*-heptane (HPLC Grade; Wako Pure Chemical Industries), toluene (Infinity Pure; Wako Pure Chemical Industries), *n*-octane, *n*-nonane, *n*-decane, methylcyclohexane, ethylcyclohexane, and isopropylcyclohexane (EP grade; Tokyo Chemical Industry) as ingredients for model naphtha.

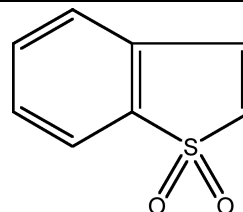
Silica gel (SIL, Davison silica gel 923), silica gel impregnated with active carbon (ACSIL; Wako Pure Chemical Industries), active carbon (AC, Diahope; Mitsubishi Chemical), silica-alumina (NBD, Neobead D; Mizusawa Industrial Chemicals), and molecular sieve 13X (MS; GL Sciences) were used as adsorbents (Table 1).

### 2.2. Preliminary Tests

A series of preliminary test runs were made using the commercial adsorbents and a standard solution with a high sulfur concentration. The standard solution was prepared from BTDO dissolved in toluene and diluted with *n*-heptane to give a toluene concentration of 1 wt% and a BTDO concentration of 75 ppm, corresponding to a sulfur concentration of approximately 14 ppm. Each test run used approximately 100 g of the heptane solution and consisted of the following: (1) adding 20 mg of adsorbent (Table 1) that had been activated by drying, agitating for 10 min, and leaving for 50 min; (2) a 1-ml aliquot of the solution was then removed for analysis and an additional 20 mg of adsorbent was added to the remaining solution. This procedure was repeated six times. The BTDO concentration in the sample was measured by HPLC using UV detection. The analytical column consisted of a Nucleosil 50-5 silica gel column (i.d. 2.0 mm, length 250 mm), using an eluent mixture of *n*-hexane/ethanol (7 : 3 vol/vol) at a flow rate of 2 ml/min. The sample size was 20  $\mu\text{l}$  with

Table 2 Composition of a Model Naphtha for Screening Test II

Composition	Concentration
Methylcyclohexane	15 wt%
<i>n</i> -Heptane	13 wt%
Ethylcyclohexane	24 wt%
<i>n</i> -Octane	7 wt%
Isopropylcyclohexane	15 wt%
<i>n</i> -Nonane	15 wt%
<i>n</i> -Decane	10 wt%
Toluene	1 wt%
BTDO	5 ppm



Benzothiophene-1,1-dioxide (BTDO)

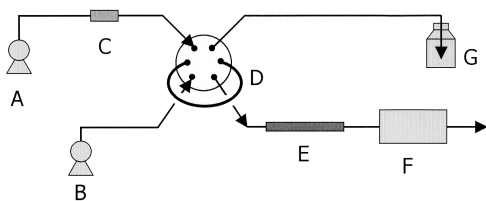
BTDO observed at a wavelength of 300 nm. The criterion used in this preliminary test was taken as 1 ppm.

The initial sulfur content of 10 ppm corresponds to the standard for "sulfur free." Previous experience led us to expect that SIL would adsorb about 5-7 wt% of the BTDO, leaving 0-5 ppm of sulfur in the remaining solution. This is why the criterion was set at 1 ppm.

### 2.3. Screening Tests

The adsorbents were screened using model naphtha with a very low sulfur concentration. This model naphtha was prepared by adding the standard BTDO-toluene solution to a mixture of alkanes and cycloalkanes (Table 2) to give a final toluene concentration of 1 wt% and a BTDO concentration of approximately 5 ppm, *i.e.*, a sulfur concentration of approximately 1 ppm.

For screening purposes, a continuous-flow adsorption test unit was used (Fig. 1), which consisted of a commercial guard column (C in Fig. 1) charged with approximately 70 mg of adsorbent, dried overnight under a stream of nitrogen (50 ml/min) at 130 $^{\circ}\text{C}$  (SIL and ACSIL) or 300 $^{\circ}\text{C}$  (MS). The model naphtha was fed from a feed pump (A) at 0.3 ml/min and, after passing



A Feed pump      B Analytical pump      C Adsorption column  
D Sampling valve      E Analytical column      F UV detector  
G Receiver

Eluent: 30 vol% ethanol/*n*-hexane.

Flow rate: 0.3 ml/min.

Analytical column: Inertsil 3, 2.1 mm I.D. × 250 mm.

Sampling loop: 20  $\mu$ l.

Wave length of UV detector: 300 nm.

Fig. 1 Schematic Diagram of Continuous-flow Adsorption Test Unit

through the adsorption column, was sampled every 20 min using valve D in Fig. 1. Each sample was analyzed by HPLC using the same procedure as in the preliminary runs. The BTDO concentration in the effluent was measured using a UV detector. The detection limit in this system was approximately 5 ppb for BTDO, or approximately 1 ppb sulfur. The BTDO concentration in the recovered naphtha was estimated by integrating the BTDO concentration curve with time.

The criterion used for evaluation was taken as the throughput per 1 g of adsorbent necessary for the sulfur concentration to reach 10 ppb in the recovered naphtha.

### 3. Results and Discussion

In general, industrial adsorbents require (1) a high adsorption throughput, adsorbing power, and adsorption rate, (2) the ability to be recycled efficiently for reuse, (3) minimal interference from other ingredients, and (4) low cost. Five commercial adsorbents were evaluated in a preliminary test: SIL, ACSIL, AC, NBD and MS (Fig. 2). MS, ACSIL, and SIL met our criteria, while NBD and AC did not. The BTDO concentrations adsorbed by MS, ACSIL, and SIL ranged between 5 and 7 wt%. NBD resembles MS in being highly acidic, but its adsorption rate is generally too slow for practical application. AC has a large specific surface area of 1000 m<sup>2</sup>/g or greater, but had limited absorption efficiency and polarity seemed to be more important than specific surface area for the adsorption of BTDO under the experimental conditions.

Figure 3 shows the correlation between the sulfur concentration in the recovered naphtha and the throughput per g of adsorbent found on screening the model naphtha with its sulfur concentration of approximately 1 ppm. Of the three adsorbents that proved suitable in the preliminary test, SIL proved to have the best perfor-

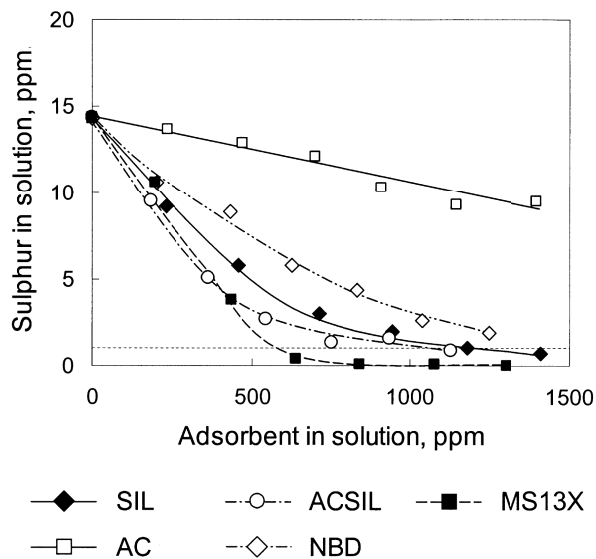


Fig. 2 Adsorption Performance of Adsorbent on the Preliminary Test

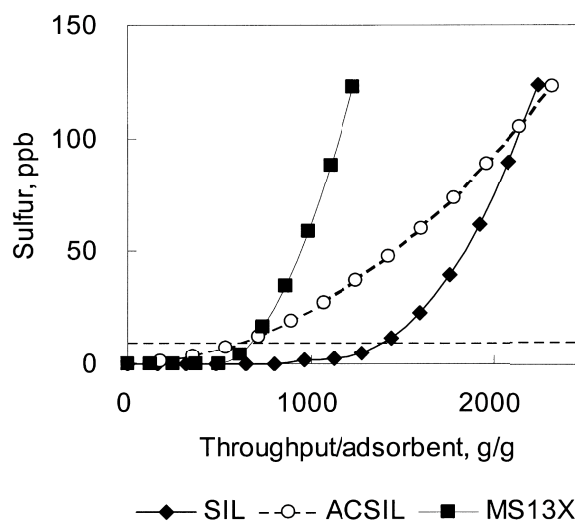


Fig. 3 Profiles of Sulfur Contents Using Selected Adsorbents on the Screening Test

mance, and the sulfur level in the recovered solution fell below 10 ppb when the throughput reached approximately 1300 g/g-adsorbent. The sulfur level remained relatively constant as the throughput was increased to approximately 1300 g/g-adsorbent, but subsequently began to increase rapidly. The concentration of BTDO adsorbed was approximately 0.5 wt% when the sulfur level of the collected naphtha reached 10 ppb.

Both MS and ACSIL deviated from the criterion when the throughput reached approximately 600 g/g-adsorbent. SIL proved the most effective adsorbent in the screening, unlike the result found in the preliminary runs, and these results indicate that the likely per-

formance of an adsorbent in an extremely dilute solution cannot be assessed based on its behavior under standard conditions.

The profiles in **Fig. 3** suggest that SIL has a few strong adsorption sites that cannot be identified using standard procedures. However, SIL has a wide distribution of pore diameters. Some pores are of an optimum diameter to allow the adsorption of BTDO by caging, rather than as a result of polarity effects. MS probably has fewer such pores than SIL. Conversely, caging does not appear to play any role in the activity of ACSIL given that its profile in **Fig. 3** corresponds to Henry's law.

#### 4. Conclusion

Five commercial adsorbents (SIL, ACSIL, AC, NBD and MS) were evaluated for possible use in post-ODS treatment of naphtha, by examining how well they adsorbed BTDO from a model naphtha solution.

In a preliminary test, SIL, ACSIL and MS proved effective in reducing the sulfur content from 14 ppm to 1 ppm, while AC and NBD failed to lower the sulfur content to 1 ppm. In screening tests, however, SIL had the highest throughput while reducing the sulfur content from 1 ppm to a target value of 10 ppb. Approximately 1300 g of the model naphtha could be processed through 1 g of fresh SIL, while only approxi-

mately 600 g could be processed per gram of either MS or AC.

Overall, SIL proved the best adsorbent out of the five commercial adsorbents for producing "Hyper-Clean Naphtha."

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## 要 旨

### ナフサ中の極微量硫黄酸化物の吸着分離—吸着剤のスクリーニング—

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酸化脱硫により生成した硫黄酸化物をナフサ中から吸着分離するための吸着剤のスクリーニング試験をベンゾチオフェン-1,1-ジオキソド (BTDO) をモデル硫黄化合物として実施した。

予備試験では硫黄濃度約 14 ppm の BTDO-モデルナフサ溶液を用いて, 硫黄濃度 1 ppm をモデルナフサの 0.2 wt% 以下の量で達成する吸着剤を探索した。その結果, シリカゲル (SIL), 活性炭埋蔵シリカゲル (ACSIL), モレキュラーシーブ (MS13X)

は 1 ppm 以下を達成したが, 活性炭およびシリカアルミナ系吸着剤は 1 ppm を達成できなかった。

次に, 予備試験で選定した 3 種類の吸着剤について, 流通式吸着試験装置を用い, 硫黄濃度 10 ppb 以下を維持する処理量を比較することにより吸着剤の性能を評価した。その結果, SIL の吸着剤 1 g あたりの処理量は 1000 g 以上となり, 最も高性能な吸着剤であった。