

## Tetrahydrothiophene(THT)의 흡착 제거

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### Adsorptive removal of tetrahydrothiophene(THT)

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#### Introduction

Tetrahydrothiophene(THT) is one of widely-used odorants in city gas mainly composed of natural gas. Recently, fuel cells have attracted much interest especially as an environmental-friendly power source in which dihydrogen and dioxygen converted into water while producing heat and electricity. There are several types of fuel cell having different operating temperatures and fuel sources. One of strategies for fuel cell applications is to utilize natural gas in city gas as a hydrogen source. To do this, a couple of processes are in need. Generally, following units are connected in series prior to the polymer electrolyte membrane fuel cell (PEMFC); (1) a unit for steam-reforming reaction, (2) a unit for water-gas shift reaction, (3) a unit for removal of residual CO. Sulfur compounds present in city gas can cause severe deactivation in catalysts for above reactions even with very low concentrations. Therefore, complete removal of sulfur compounds is in order. Two different methods have been generally studied. One is the high-temperature catalytic desulfurization with dihydrogen over supported metal sulfide catalysts. The other is the low-temperature adsorption. Commercial bulk petroleum industry generally utilizes the former process where organic sulfur compounds are transformed into elemental sulfur. Although this unit is proven technology, it needs high temperature to sustain hydrogenation reaction. Usually, adsorption is regarded as a more effective method for deep desulfurization than is HDS. Roh et al [1] have investigated the adsorptive desulfurization of natural gas for fuel cells. They utilized various adsorbents such as activated carbon (AC), Fe/AC, BEA zeolite(BEA), and Fe/BEA for the adsorption of *tert*-butyl mercaptan (TBM) and tetrahydrothiophene(THT). They found that Fe/BEA prepared by the ion-exchange method exhibited the highest sulfur capacity (19.6%g-comp./g<sub>sorb</sub>) among the adsorbents tested and interpreted this result with the possibility that strong chemisorption could be occurred on the Lewis acid sites and that sulfur compounds could be combined with Fe. Yang et al [2] reported that Cu<sup>+</sup> and Ag<sup>+</sup> zeolite Y could adsorb sulfur compounds from commercial fuels selectively and with high sulfur capacities (by  $\pi$ -complexation) at ambient temperature and pressure. For Cu+zeolites, the vapor phase exchange method was also successfully applied [3]. The theoretical calculation on  $\pi$ -complexation was performed [4]. The multi-layered bed system composed of activated carbon and transition metal ion-exchanged zeolites has been proposed as an advanced system [5]. Mckinley and Angelici [6] utilized silver salts adsorbed on amorphous silica or mesoporous SBA-15 to extract dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene(4,6-Me<sub>2</sub>DBT) from simulated, hydrotreated petroleum feedstocks. Hernandez-Maldonado and Yang [7] reported that Ni(II)-exchanged X-and Y-zeolite could be utilized as adsorbents for sulfur compounds from diesel fuels by  $\pi$ -complexation. Until now, most adsorptive deep desulfurization studies have been conducted to remove organic sulfur compounds containing benzene derivatives in the liquid phase. To utilize city gas as a hydrogen source, studies on adsorptive removal of simple organic sulfur compounds in the gas phase should be carried out. In this report, THT was selected as a model compound and its adsorptive removal was performed over various

materials. Characteristics of adsorption and desorption is correlated with physical and chemical properties of adsorbents via some characterization techniques.

### Experimental

BEA zeolite, zeolite Y, and mordenite were purchased from Zeolyst International. BEA zeolite is an ammonium ion-exchanged beta type zeolite (CP814E) with a surface area of 680 m<sup>2</sup>/g. The molar ratio of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> is 25. Zeolite Y (CBV100) is a sodium ion-exchanged material with a surface area of 900 m<sup>2</sup>/g, in which the molar ratio of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> is 5.1. Mordenite (CBV 21A) is a ammonium ion-exchanged zeolite with a surface area of 500 m<sup>2</sup>/g, where the molar ratio of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> is 20. Ag<sup>+</sup>-zeolite Y was prepared by an ion-exchange method with zeolite Y (CBV100) and an aqueous solution of silver nitrate. The weight percent of ion-exchanged silver was 22.2. Ordered mesoporous carbon was prepared by a replica method from SBA-15 and carbon precursors. Natural zeolite and montmorillonite was purchase from Wangpyo Chem. and Sigma-Aldrich, respectively. Total amounts of THT over various adsorbents were measured by a pulse adsorption method with Autochem 2910 (Micromeritics). All adsorbents were pretreated with helium at a flow rate of 10 ml/min at 673 K for 1 h. Manual injections of 1 μl of liquid THT were conducted at 303 K with a micro syringe until no further adsorption was observed while helium was allowed to flow through the sorbent at a rate of 30ml/min. After saturating the adsorbent with THT, the temperature programmed desorption (TPD) was conducted with helium at a rate of 30ml/min from 303 K to 673 K at a ramping rate of 10K/min. The effluent gas was monitored with a thermal conductive detector (TCD).

### Results and Discussion

THT adsorption was performed over BEA zeolite (Si/Al=25). 1 μl of liquid THT was injected manually over 30 mg of adsorbent periodically and its effluent concentration of THT was monitored as shown in Fig. 1.

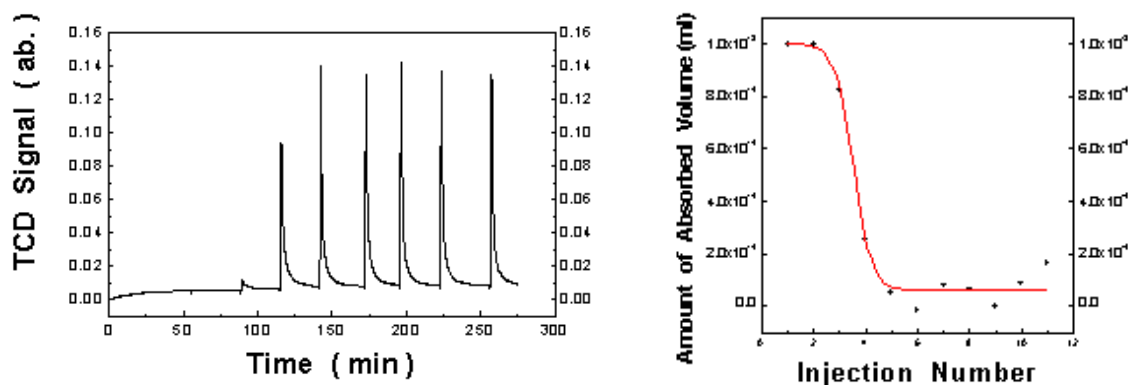


Figure 1. TCD signal with time on stream (left) and the amount of THT adsorbed with injection times (right) over BEA zeolite.

This data can be converted to the adsorbed THT per injection as shown in Fig.1. Total adsorbed THT can be calculated by summing each amounts of THT adsorbed. TPD was conducted to find out the adsorption strength. Weak and mild adsorption could be found between 303 K and 473 K in TPD pattern as shown in Fig.2. The small desorption peak at 600K can be due to strong adsorption between THT and defect sites of BEA zeolite.

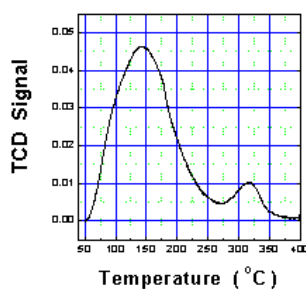
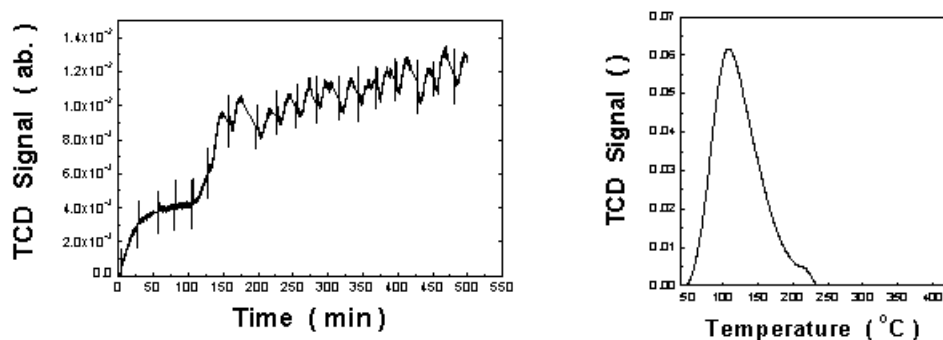
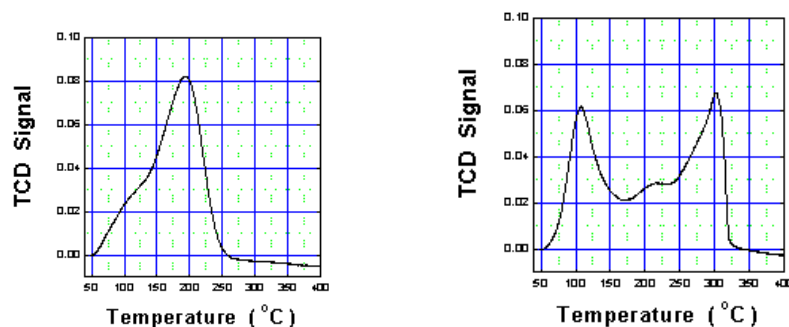


Figure 2. TPD patterns with temperatures over BEA zeolite.

The ordered mesoporous carbon with a high surface area of  $1500\text{m}^2/\text{g}$  was tested. The gradual increase in TCD signal caused by reversible adsorption of THT at 303K was observed when manual injections were performed as shown in Fig.3. Therefore, adsorbed THT over this carbon material cannot be calculated by a pulse adsorption method. Weak and moderate adsorption strength can be confirmed by TPD patterns as shown in Fig.3.

Figure 3. TCD signal with time on stream (left) and TPD patterns with temperature (right) over mesoporous carbon with a high surface area of  $1500\text{ m}^2/\text{g}$ .

THT adsorption was conducted over zeolite Y and  $\text{Ag}^+$ -zeolite Y. Each adsorbent retained 0.166 and 0.208 g of THT per g of adsorbent, respectively. This result showed that there existed a positive effect on adsorption of THT through silver ion-exchange. TPD patterns of these two adsorbents are shown in Fig. 4. Strong desorption peak at a high temperature was observed over  $\text{Ag}^+$ -zeolite Y. This can be interpreted that silver ion can present new sites for a strong adsorption.

Figure 4. TPD patterns with temperatures over zeolite Y (left) and  $\text{Ag}^+$ -zeolite Y (right).

Total amounts of adsorbed THT over various adsorbents are listed in Table 1. Natural zeolite and montmorillonite has very small capacity for the adsorption of THT. Mordenite was found to have some sites for THT adsorption.

Table 1. Amounts of adsorbed THT over various adsorbents

adsorbents	Amounts of adsorbed THT (gTHT/gsorb)
BEA Zeolite	0.116
Mordenite	0.088
Zeolite Y	0.166
Natural zeolite	0.003
Montmorillonite	0.006

### Conclusion

Different adsorption and desorption features of THT were observed over various adsorbents. Weak physical adsorption was dominant over carbon supports and some molecular sieves whose pore sizes were less than kinetic diameter of THT. However, moderate adsorption was found over zeolites whose average pore sizes were larger than kinetic diameter of THT. Strong adsorption site could be made by Ag<sup>+</sup>-exchange.

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