Removal of Tetrahydrothiophene by an Adsorpton Method

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Introduction

Fuel cells are efficient and environment-friendly electric power generation systems by the electrochemical reactions of H_2 and O_2. Hydrogen can be formed from a variety of hydrocarbons such as natural gas, gasoline, and methanol via catalytic reforming. However, the production of fuel cell grade hydrogen is complicated task due to the stringent requirements in its quality [1]. The removal of sulfur compounds from the fuels is markedly important, because sulfur poisons, even with very small concentrations, the reforming catalysts and fuel cell electrodes, resulting in significant decreases in their activities. Recent studies have shown that adsorptive removal of thiophene and alkyl-thiophene from liquid fuels can be effectively carried out using the metal ion-exchanged Y-zeolites such as Ag-Y and Cu-Y via specific π-interactions [2,3]. However, only a few studies [4,5] have been reported on the removal of organic sulfur compounds from natural gas, while it is considered as one of the most effective H_2 source for fuel cells. Here, we report the adsorptive removal of tetrahydrothiophene (THT, C_4H_8S) at ambient temperatures and pressure using various adsorbents; BEA, Mordenite, Na-Y, and Ag-Y zeolites. THT was selected as a model compound, because it is widely used as an odorants in natural gas. The adsorption capacities and characteristics were correlated with the structural properties of the adsorbents. In addition, the THT adsorption capacity of Ag-Y zeolites was discussed according to the preparation methods, level of Ag ion-exchange, and their relative crystallinity.

Experimental

BEA zeolite, Y-zeolite, and mordenite samples were purchased from Zeolyst International. The BEA zeolite (SiO_2/Al_2O_3 = 25) was an ammonium ion-exchanged beta type form (CP814E) with the surface area of 680 m^2/g. The Y-zeolite (CBV100, SiO_2/Al_2O_3 = 5.1) was a sodium ion-exchanged material with the surface area of 900 m^2/g. The mordenite (CBV 21A, SiO_2/Al_2O_3 = 20) was an ammonium ion-exchanged form with the surface area of 500 m^2/g. Ag-Y zeolites were prepared by various routes. The initial Na-Y was transformed into NH_4^+-Y or H-Y by an ion-exchange with 1M NH_4NO_3 aqueous solution (25ml solution per gram sample). The samples were dried at 383K for 16 h to obtain NH_4-Y. In order to form H-Y, the NH_4-Y was calcined in flowing dry air at 673 K for 4 h. Finally, Ag-Y samples were obtained by an ion-exchange of the Na-Y, NH_4-Y, and H-Y with Ag ions in aqueous solutions of silver nitrate (0.05 - 0.1 M) at 298 K for 3 h, respectively. After then, the samples were dried at 383 K for 16 h, and calcined in flowing dry-air at 673 K for 4 h. The extent of Ag ion-exchange was calculated using the metal composition obtained by ICP analysis. The crystallinity of these samples were calculated (ASTM, D3906-03) from the X-ray powder diffraction results obtained

using Philips X'pert-MPD unit with Cu-K$_\alpha$ radiation (λ=1.54056 Å) at 40 kV and 30 mA. The THT adsorption capacities of the adsorbents were measured by a pulse adsorption method at 303 K and atmospheric pressure using Autochem 2910 (Micromeritics). The adsorbents (30 mg) were placed in the sample tube and pretreated in flowing dry helium at 673 K for 1 h (ramp:10 K min^{-1}). Manual injections of THT (1 μl for each injection) into the He carrier gas flow steam (50 ml min^{-1}) was conducted at 303 K until no further adsorption was observed. Upon the completion of THT adsorption, the temperature programmed desorption (TPD) was conducted in a dry-helium flow (30ml min^{-1}) by raising temperature from 303 to 673 K with a ramping rate of 10 K min^{-1}. The effluent was monitored using thermal conductivity detector (TCD).

Results and Discussion

The THT adsorption capacities of Na-Y, BEA, and mordernite samples are displayed along with their structural properties in Table 1. The Na-Y zeolite showed the highest adsorption capacity followed by BEA, and mordenite. Considering the molecular size of THT (5.3 x 3.5 Å) and the pore dimensions of the adsorbents, it appears that adsorbents with pore dimensions larger than the molecular size of THT offer high adsorption capacities. It is reasonable that accommodation of adsorbate molecules of the size compatible or larger than the sorption sites of adsorbents would be restricted. In the case for Na-Y zeolite, the fraction of large sorption sites is presumably high, and this results in the high sorption capacity for THT. Conversely, a significant fraction of the sorption sites in mordenite is smaller than the THT molecules, resulting in the low THT adsorption capacity.

Table 1. THT adsorption capacities of the adsorbents

Adsorbent	THT adsorption capacity (mmol/g-adsorbent)	Pore size (Å)	Surface Area (m^2/g-adsorbent)
Na-Y	1.88	7.4 x 7.4	900
BEA	1.32	6.5 x 5.6 7.5 x 5.7	680
Mordenite	0.74	5.7 x 2.6 7.0 x 6.5	500

A moderate incorporation of Ag-ions in the framework of Y-zeolite resulted in an increase in THT adsorption. Figure 1 shows the THT adsorption capacity as a function of the level of Ag ion-exchange. The values in parenthesis are relative crystallinity of the Ag-Y samples with respect to the Na-Y zeolite. As can be seen, the THT adsorption amount initially increased as the amount of Ag ions increased, reaching a maximum of 2.99 mmol THT per gram adsorbent at 32 % of the ion-exchange level. However, a further incorporation of silver ions resulted in an adverse effect showing a decrease in the THT adsorption capacity. It is clear from the results that the THT adsorption capacity of Ag-Y does not show a monotonous correlation with Ag ion-exchange level. Another crucial factor for a high sorption capacity would be crystallinity of the adsorbents as can be deduced from the crystallinity values displayed also in Figure 1. In order to investigate the effects of crystallinity and Ag cation-exchange level on the THT adsorption capacity, the Ag ion-exchange was conducted with various cation forms of Y
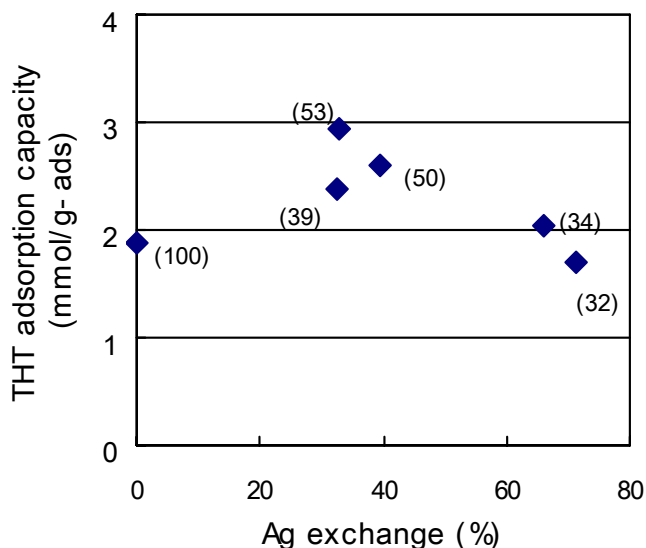
zeolites; NH_4-Y, H-Y, and Na-Y.

Figure 1. Adsorption amounts of THT over Ag-Y zeolites of various Ag ion exchange level. The value in parenthesis shows crystallinity (%). The samples were formed from Na-Y zeolites

As shown in Table 2, the crystallinity of Ag-Y could be varied according to the inherent cation type of Y zeolite precursor. Ag-Y samples derived from Na^+ form of Y zeolite showed much higher THT adsorption capacities than those obtained from NH_4^+ and H^+ form of Y zeolites. Furthermore, a pre-calcination of Na-Y zeolites (air, 773 K for 4 h) before Ag ion-exchange resulted in a significant improvement in the THT adsorption capacity (Ag-Y(A)), even with a low Ag cation exchange level, due to an enhancement in its crystallinity. In the case of Ag-Y (E, F), high Ag cation exchange levels were achieved by carrying out the ion-exchange twice. However, a concurrent decrease in the crystallinity effected more significantly on the THT adsorption, resulting in a lower adsorption capacities of Ag-Y (E, F) than those of Ag-Y (A, B).

Table 2. THT adsorption capacities of the Ag-Y zeolites prepared from various cation forms[a].

Adsorbent	Cation form	Ag Cation Exchange (%)	Crystallinity (%)	THT adsorption capacity (mmol/g-adsorbent)
Na-Y	Na^+	0	100.0	1.88
Ag-Y (A)	Na^+	32.8	53.9	2.99
Ag-Y (B)	Na^+	39.4	50.0	2.65
Ag-Y (C)	NH_4^+	32.7	45.3	2.40
Ag-Y (D)	H^+	24.2	36.9	1.70
Ag-Y (E)	Na^+	66.1	29.0	2.37
Ag-Y (F)	Na^+	68.2	32.3	2.36

[a] Ag-Y (A-D) were ion-exchanged with Ag ion once, Ag-Y(E, F) were ion-exchanged with Ag ion twice. Especially, Ag-Y (A, E) was pre-calcined under air flow at 673 K for 4 h before carrying

out Ag ion-exchange.

Conclusions

In this work, we studied THT adsorption capacities of mordenite, Na-Y, Ag-Y and BEA zeolites at ambient temperature and pressure.   The pore dimension of these adsorbents was the primary factor that effected on the amount of THT adsorption, in which the adsorption capacity showed an order following Na-Y> BEA > mordenite corresponding to the size of sorption sites.   In the case for Ag-Y zeolites, both Ag-exchange level and the crystallinity were important factors for THT adsorption.   A high THT adsorption capacity could be achieved even with a low Ag ion-exchange level, when the crystallinity was high.

References

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