

## Adsorptive Removal of Tetrahydrothiophene in a Pipeline Natural Gas

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### Introduction

The city gas mainly composed of natural gas can be a promising hydrogen source for the distributed fuel cell system. For safety, some organosulfur compounds such as *tert*-butylmercaptan (TBM), dimethylsulfide (DMS) and tetrahydrothiophene (THT) should be added in a city gas and these odorants should be removed before a fuel processor not to cause the catalyst deactivation. Although the conventional catalytic hydrodesulfurization (HDS) is a well-proven technology, it is not plausible for the small-scale fuel cell system. Therefore, the adsorptive removal of sulfur compounds has been intensively examined [1-4]. In the previous works [2-4], we examined the adsorption of THT and TBM on AgNa-Y zeolites and found that an introduction of Ag in Na-Y via a cation exchange did not increase the breakthrough THT adsorption uptake noticeably, whereas it significantly enhanced the breakthrough TBM adsorption uptake. We also found that adsorption of THT and TBM appeared to compete on the adsorption sites, while the adsorption strength of THT was much higher than that of TBM. As a consequence, AgNa-Y showed an almost 100 % total adsorption selectivity for THT over TBM regardless of the Ag<sup>+</sup> exchange level when these two sulfur species coexisted in the feed stream. This experimental result was also supported by the density functional theory calculation study in which the order of binding energies of sulfur compounds were determined to be THT > DMS > TBM > H<sub>2</sub>S > COS [3]. Furthermore, we also observed the formation of Ag-S bond with concomitant decreasing the interaction between Ag<sup>+</sup> and oxygen in the lattice as well as the interaction of Ag-Ag in the metallic Ag during the adsorption of THT at ambient temperature with an X-ray absorption spectroscopy (XAS) [4]. In this work, we prepared some transition metal-ion-exchanged Na-Y adsorbents and examined the adsorption and desorption characteristics of THT.

### Materials and Methods

A powder form of Na-Y zeolite (320NAA, Tosoh Co., Japan, the molar ratio of Si/Al=2.81) was used as the precursor for metal ion-exchanged Y (MNa-Y) zeolites. The conventional ion-exchange method was adopted to prepare MNa-Y from an aqueous metal nitrate solution. After an ion-exchange procedure, the slurry containing MNa-Y was filtered and MNa-Y was rinsed with the deionized water several times and dried at 383 K overnight. Finally, MNa-Y zeolites were pretreated at 773 K for 4 h with dry air.

Sulfur uptake on the adsorbents was measured at 303 K and atmospheric pressure using a small fixed bed reactor with adsorbents. A feed gas of 100 ppm THT balanced with CH<sub>4</sub> was fed to the reactor, in which 0.10 g of adsorbents was charged, at a flow rate of 55 ml / min. The effluent from the reactor was analyzed by gas chromatograph (Donam, DS6100) with a pulsed

flame photometric detector (PFPD) and a flame ionization detector (FID). The breakthrough uptake and the total uptake were obtained as described in our previous works.

The nitrogen physisorption, an inductively coupled plasma-atomic emission spectroscopy (ICP-AES), the temperature programmed desorption (TPD) of THT and X-ray diffraction (XRD) were conducted to characterize the materials.

### Results and Discussion

The total uptake and the breakthrough uptake decreased as the following order: AgNa-Y > Na-Y > CuNa-Y > CoNa-Y > NiNa-Y. The interaction between THT and an adsorbent can be probed with the temperature-programmed desorption (TPD) technique after adsorption of THT on the adsorbent. Based on the TPD patterns determined with the thermal conductive detector as well as the mass spectroscopy, the interaction between THT and metal ions in MNa-Y decreased as the following order: Co<sup>2+</sup> > Ag<sup>+</sup> ~ Cu<sup>+</sup> > Ni<sup>2+</sup> > Na<sup>+</sup> > H<sup>+</sup>. Some of THT were decomposed into C<sub>4</sub>H<sub>8</sub> and H<sub>2</sub>S over MNa-Y during the TPD experiment. C<sub>4</sub>H<sub>8</sub> desorbed at the same temperature with THT, but some of H<sub>2</sub>S still adsorbed at low temperatures and desorbed at high temperatures.

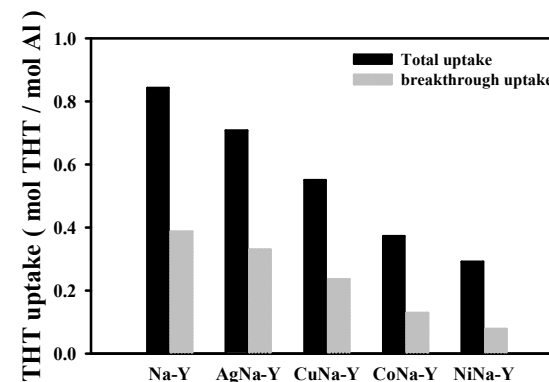


Figure 1. The breakthrough uptake and the saturation uptake of THT on Na-Y, AgNa-Y, CuNa-Y, CoNa-Y and NiNa-Y.

### Significance

The interaction between the metal cation in MNa-Y and tetrahydrothiophene (THT) was examined to find a proper adsorbent to remove THT in a pipeline natural gas with an adsorption method.

### References

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