

## 마이크로세공 분자체를 이용한 탄화수소에 포함된 황화물의 선택적 제거

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### Selective Removal of Sulfur Compounds in Hydrocarbon using Microporous Molecular Sieves

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#### INTRODUCTION

Desulfurization of pipeline natural gas fuel at ambient conditions before introduction to reforming processes is strongly needed for stationary source application of fuel cells, such as polymer electrolyte fuel cells (PEFC). The sulfur content of pipeline natural gas in the Korea is 4 to 7 ppm and usually contains TBM, THT and trace amounts of H<sub>2</sub>S. Sulfur compounds, present as odorants, are poisons for many downstream catalysts especially for the anode. They are also poisons for any metal oxide catalysts present in the process for the production of hydrogen [1-3].

The objective of this study is to examine ion-exchanged zeolites, specifically Y zeolites, to remove sulfur compounds (THT and TBM) from natural gas at 30 °C and normal pressure using fixed-bed adsorption-breakthrough techniques with gas chromatography-flame ionization detection (GC-FID) and gas chromatography-flame photometric detection (GC-FID). Additionally, the adsorption behaviors and the sulfur capacities for removal of THT and TBM were analyzed by means of temperature programmed desorption (TPD) and mass spectroscopy.

#### EXPERIMENTAL

The adsorption runs were carried out in at 30 °C and normal pressure on standard gas comprised of 29.4 ppmv TBM and 69.7 ppmv THT on methane balance passed through with flow rate of 50 cc/min.

Concentrations of TBM and THT in the inlet and outlet gases were analyzed by a gas chromatograph (HP- 5890) equipped with a packed column of OV 101 and a flame ion detector (FID).

After adsorption run, desorption run was carried out with the temperature elevated from 30–500 °C at a rate of 10 °C/min in He 50 cc/min. The compounds desorbed in TPD runs were analyzed by a Mass spectrometer (HPR 20 Hiden).

## RESULTS AND DISCUSSION

The results of the adsorption experiments for zeolites ion-exchanged with many different cations in Table 1 showed that Na-Y, Ag-Na-Y and Cu-Na-Y were found to be highly effective and capable of removing sulfur compound. Sulfur adsorption capacities for Ag-Na-Y and Cu-Na-Y were 1.61 mmol-S/g and 1.38 mmol-S/g respectively. These sulfur adsorption capacities were higher than those of other adsorbents (Li-Na-Y, K-Na-Y, Fe-Na-Y, Co-Na-Y and Ni-Na-Y). These good behaviors of removal of sulfur compound for Y zeolite ion-exchanged with cations Ag and Cu probably depended on their acidity. It can be seen clearly in Fig. 2 which shows the correlation of adsorption activity and acidity of adsorbent, it showed that amount of sulfur compound THT adsorbed on M-Na-Y is linear with the area under  $\text{NH}_3$ -TPD curves. The areas under  $\text{NH}_3$ -TPD-curves in the case of Na-Y ion-exchanged with Cu and Ag are larger than Na-Y ion-exchanged with other cations Li, K, Fe, Co and Ni.

Table 1. TBM and THT adsorption capacities on cation ion-exchanged Y zeolite

Sample	Breakthrough Time (min)		Amount of sulfur compound adsorbed (mmol-S/g)	
	TBM	THT	TBM	THT
Na-Y	45	90	0.30	1.38
Li-Na-Y	30	45	0.20	0.69
K-Na-Y	15	45	0.10	0.69
Ag-Na-Y	45	105	0.30	1.61
Cu-Na-Y	45	90	0.30	1.38
Fe-Na-Y	15	15	0.10	0.23
Co-Na-Y	15	15	0.10	0.23
Ni-Na-Y	15	15	0.10	0.23

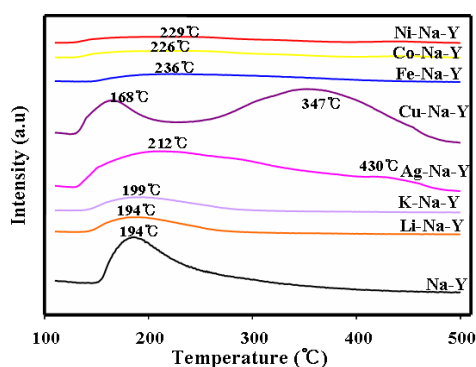


Fig. 1.  $\text{NH}_3$ -TPD spectra on M-Na-Y.

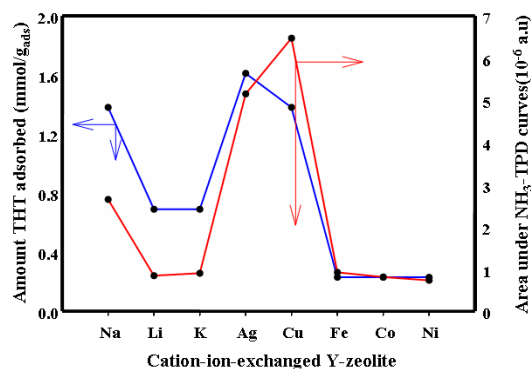


Fig. 2. Comparison of amount THT adsorbed and area obtained from  $\text{NH}_3$ -TPD.

Table 2. Effect of Cu loading in Na-Y

Sample	Breakthrough Time (min)		Total amount sulfur (Before the split time)(mmol-S/g)	Amount of sulfur compound adsorbed (mmol-S/g)	
	TBM	THT	TBM and THT	TBM	THT
Na-Y	180	240	1.99	0.59	1.87
Cu-Na-Y-0.01	150	210	1.66	0.49	1.63
Cu-Na-Y-0.05	165	225	1.82	0.54	1.75
Cu-Na-Y-0.1	240	240	2.81	0.84	1.87
Cu-Na-Y-0.2	105	105	1.16	0.34	0.82

Y zeolite ion-exchanged with cation copper had effective result in adsorptive removal of sulfur compound. Therefore, adsorption process of sulfur compound was carried out on Na-Y ion-exchanged with various content of  $\text{Cu}(\text{NO}_3)_2$  solution 0.01, 0.05, 0.1 and 0.2 M. The result of these experiments is shown in Table 2, the sulfur adsorption capacities on Cu-Na-Y slightly decreased with an increase in copper content up to 0.05M. However, in the case of Cu-Na-Y-0.1, TBM and THT were removed simultaneously with the maximum adsorption amount. TBM adsorbed on Cu-Na-Y-0.1 did not be affected by THT and total sulfur adsorption capacity for both TBM and THT was 2.81 mmol-S/g. It shows the best sulfur capacity so far in removing organic sulfur compounds from fuel gas by adsorption on zeolites. This value improved considerably compared to that of Na-Y (mmol-S/g). We also can see these cases more clearly in Fig. 3(a) and (b), showing the breakthrough curves of TBM and THT for adsorption on Na-Y and Cu-Na-Y-0.1. In case of Na-Y in Fig. 3(a), after the first detection of TBM in the outlet gas, THT was still being taken up and the C/Co values of TBM exceeded 1.0. The amount of sulfur compound adsorbed were 1.87 mmol-S/g for THT, which amount was close to the total amount of sulfur compound adsorbed on the Na-Y at the time before the split is 1.99 mmol-S/g. Otherwise, Fig. 4(a) showing TPD-spectra on Na-Y, TPD curve of TBM ( $m/e = 41$ ,  $\text{C}_3\text{H}_5$  a main fragment of TBM) with very weak peaks at 90 °C and 270 °C, and TPD curve of THT ( $m/e = 60$ ,  $\text{C}_2\text{H}_4\text{S}$  a main fragment of THT) strong peaks at 90 °C and 270 °C. It can be supposed that main adsorption site of THT is the same as that of TBM but interaction between THT and adsorption site is stronger than that of TBM on Na-Y. Therefore, The TBM molecules temporary adsorbed on Na-Y were removed at the equilibrium state likely due to replacement by THT.

On the other hand, Cu-Na-Y-0.1 in Fig. 3(b) showed total adsorption times until the breakthrough of TBM and THT in approach to 240min. In this case, TBM adsorbed on Cu-Na-Y were not affected by adsorption of THT on Cu-Na-Y. In TPD curve of Fig. 4(b), TBM shows a peak at 109 °C and THT showed a peak at 270 °C. Therefore, it can be found that adsorption site of TBM and THT are totally

different on Cu-Na-Y. Copper ion-exchanged on Na-Y generated a lot of adsorption sites which can selectively adsorb for TBM.

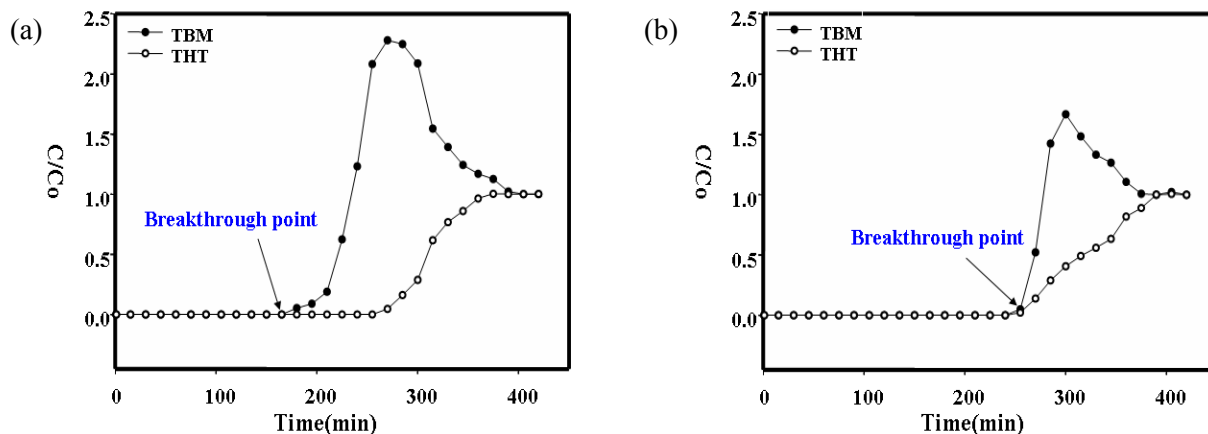


Fig. 3. Breakthrough curves of TBM and THT on (a) Na-Y and (b) Cu-Na-Y-0.1.

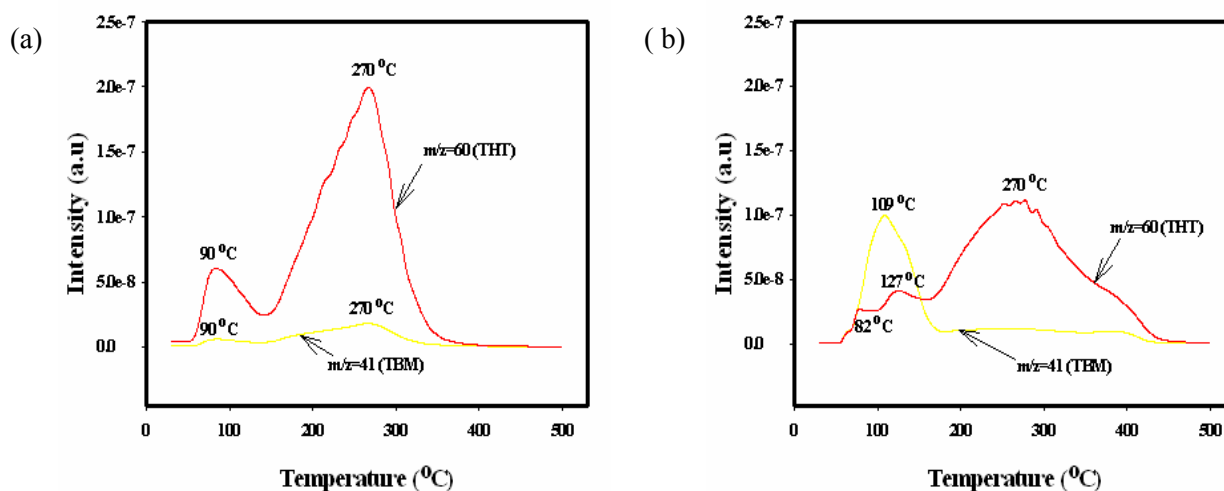


Fig. 4. TPD-spectra on (a) Na-Y and (b) Cu-Na-Y-0.1.

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