

## Selective removal of sulfur compounds in city-gas by adsorbents

Chang Hyun Ko, Hirn-Ill Song, Jong-Ho Park, Sang-Sup Han and Jong-Nam Kim<sup>†</sup>

Korea Institute of Energy Research, 71-2, Jang-dong, Yuseong-gu, Daejeon 305-343, Korea

(Received 29 August 2006 • accepted 24 April 2007)

**Abstract**—Silver nitrate impregnated on beta zeolite (BEA), mesoporous silica MCM-41 and SBA-15 ( $\text{AgNO}_3/\text{BEA}$ ,  $\text{AgNO}_3/\text{MCM-41}$ ,  $\text{AgNO}_3/\text{SBA-15}$ ) were prepared to remove sulfur compounds selectively in city-gas, which contains tetrahydrothiophene and *tert*-butylmercaptane. Sulfur adsorption capacity was determined when the sulfur concentration of effluent gas in breakthrough test reached 0.1 ppm, which is acceptable sulfur concentration for hydrogen production in a reformer for fuel cells. As the  $\text{AgNO}_3$  concentration in  $\text{AgNO}_3/\text{BEA}$ ,  $\text{AgNO}_3/\text{MCM-41}$ , and  $\text{AgNO}_3/\text{SBA-15}$  increased, their sulfur adsorption capacities also increased. Although microporous zeolite BEA has smaller pore volume and lower surface area than those of mesoporous silica MCM-41 and SBA-15, the sulfur adsorption capacity of  $\text{AgNO}_3/\text{BEA}$  was higher than those of  $\text{AgNO}_3/\text{MCM-41}$  and  $\text{AgNO}_3/\text{SBA-15}$ . Adsorbed sulfur molecules per impregnated silver nitrate and the shape change of breakthrough curves depending on the adsorption temperature showed that not only chemisorption but also physisorption was involved in sulfur compounds adsorption on  $\text{AgNO}_3$  impregnated adsorbent.

Key words: Beta Zeolite, Mesoporous Silica, Desulfurization, City-gas, Selective Adsorption

### INTRODUCTION

Considering polymer electrolyte fuel cells as house-unit power generating devices, city-gas, which can be used in steam reforming, seems to be a promising candidate for hydrogen source because the infrastructure for city-gas has been well established in Korea and Japan. Generally, sulfur compounds, such as tetrahydrothiophene (THT), tertiarybutylmercaptane (TBM) and so on, are added to city-gas for the easy detection of gas leakage. Although, the sulfur concentration of city-gas in Korea was 3.8 ppm, it must be reduced to less than 0.1 ppm prior to reforming process in order to protect reforming catalysts and fuel cell electrodes [1]. There are two basic approaches for the desulfurization of city-gas: selective catalytic oxidation and selective adsorption. Selective catalytic oxidation has attracted attention due to its lower maintenance costs and smaller facility size. However, it does require higher up-front capital investment for additional oxygen supply unit and fuel heating unit [2]. On the other hand, selective adsorption uses zeolites, metal impregnated carbons, and alumina as adsorbent at ambient temperature [3]. Thus, its simple facility set-up requires only a small amount of capital investment in reformer design. Adsorptive desulfurization has been widely applied not only for city-gas, but also for transportation fuel and synthetic gas [4-6]. In previous reports, silver ion exchanged Y zeolite ( $\text{Ag/Y}$ ) has attracted major attention as the adsorbent for selective adsorption of sulfur compounds in city-gas [7-9]. These reports claimed that high adsorption capacity (42.4 mg S/g adsorbent) and selectivity of  $\text{Ag/Y}$  for sulfur compounds are mainly attributed to acid sites and silver ion incorporated in Y zeolite. Herein, we prepared adsorbents, which selectively adsorb sulfur com-

pounds in city-gas, by impregnation of silver nitrate on beta zeolites ( $\text{AgNO}_3/\text{BEA}$ ) and mesoporous silica SBA-15 and MCM-41 ( $\text{AgNO}_3/\text{SBA-15}$  and  $\text{AgNO}_3/\text{MCM-41}$ ). The sulfur adsorption capacity of each adsorbent was measured by breakthrough test with the simulated city-gas containing THT and TBM. Sulfur adsorption amount per one unit of  $\text{AgNO}_3$  molecule and its dependency on adsorption temperature showed that the adsorption of sulfur compounds on adsorbents was controlled by physisorption in addition to chemisorption.

### EXPERIMENTAL

#### 1. Preparation of Adsorbent

MCM-41 and SBA-15 were synthesized by methods reported elsewhere [10,11]. Ammonium type beta zeolite ( $\text{NH}_4\text{-BEA}$ ) (CP-814E,  $\text{Si/Al}=50$ ) was obtained from Zeolyst.  $\text{NH}_4\text{-BEA}$  was calcined in oxygen environment at 823 K to produce hydrogen type beta zeolite (H-BEA). On these substrates (H-BEA, MCM-41, SBA-15), silver nitrate ( $\text{AgNO}_3$ ), purchased from Junsei, was impregnated by incipient wetness method. Silver nitrate impregnated substrates ( $\text{AgNO}_3/\text{BEA}$ ,  $\text{AgNO}_3/\text{MCM-41}$ ,  $\text{AgNO}_3/\text{SBA-15}$ ) were dried at 303 K in an oven for 4 hours. Then, the resulting samples were stored in air-tight container for further use.  $\text{AgNO}_3$  loading of each sample, confirmed by inductively coupled plasma atomic emission spectroscopy, was 4.8, 9.1, 16.7 wt%.

#### 2. Breakthrough Test and Sulfur Concentration Measurement

The experimental set-up of the breakthrough test for the simulated city-gas is shown in Fig. 1. The weight of adsorbent loaded on the stainless steel tube was 0.3 g. The pellet size of adsorbent was around 300 mesh. Gas flow was controlled by a mass flow meter and the flow rate was 200 sccm. Before breakthrough test,  $\text{AgNO}_3/\text{BEA}$ ,  $\text{AgNO}_3/\text{MCM-41}$ ,  $\text{AgNO}_3/\text{SBA-15}$  were activated in nitrogen environment at 373 K for 2 hour with the same flow rate. Sulfur concentration of effluent gas was measured by a total sulfur analyzer

<sup>†</sup>To whom correspondence should be addressed.

E-mail: jnkim@kier.re.kr

<sup>\*</sup>This work was presented at the 6<sup>th</sup> Korea-China Workshop on Clean Energy Technology held at Busan, Korea, July 4-7, 2006.

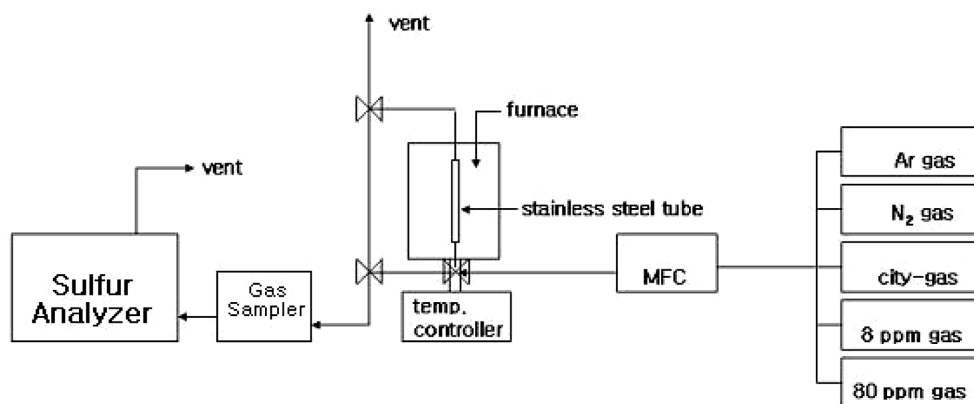


Fig. 1. Schematic diagram of experimental apparatus used in this study.

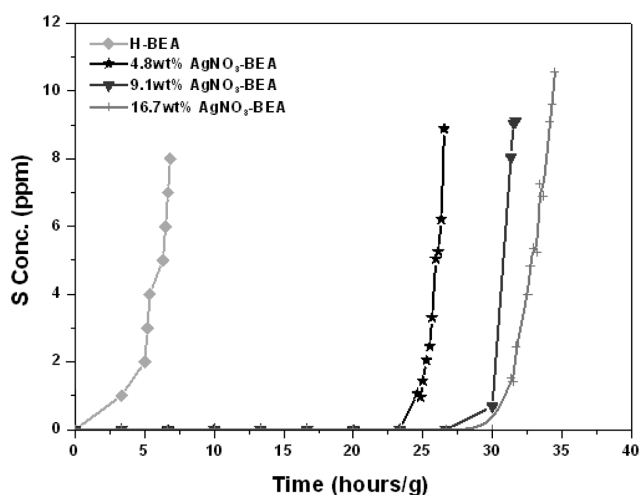


Fig. 2. Breakthrough curves for simulated city-gas: The change of breakthrough time depending on the loading of  $\text{AgNO}_3$  on adsorbent (The weight of each sample was fixed for 0.3 g): (●) BEA, (★) 4.8 wt%  $\text{AgNO}_3/\text{BEA}$ , (▼) 9.1 wt%  $\text{AgNO}_3/\text{BEA}$ , (+) 16.7 wt%  $\text{AgNO}_3/\text{BEA}$ .

(Antek 9000LLS). 734A gas sampler was attached on the Antek 9000LLS for sampling feed gas and effluent gas treated by adsorbents.

### 3. Feed Gas Composition

Simulated feed gas was provided by the Ri-gas. The total sulfur concentration of simulated gas was 80 ppmv (volume/volume): 56 ppmv THT, 24 ppmv TBM, and balanced methane.

## RESULTS AND DISCUSSION

Fig. 2 shows the sulfur compounds breakthrough curves with H-BEA and  $\text{AgNO}_3/\text{BEA}$  as adsorbents with different  $\text{AgNO}_3$  concentration. In this experiment, we tried to separate sulfur compounds and methane using the difference of adsorption strength between adsorbent-methane and adsorbent-sulfur compounds. In the breakthrough curves as shown in Fig. 2, sulfur concentration in effluent gas, treated by adsorbent, changed according to the breakthrough time. There were negligible changes of sulfur concentration in the initial part of the breakthrough curves. However, they increased ab-

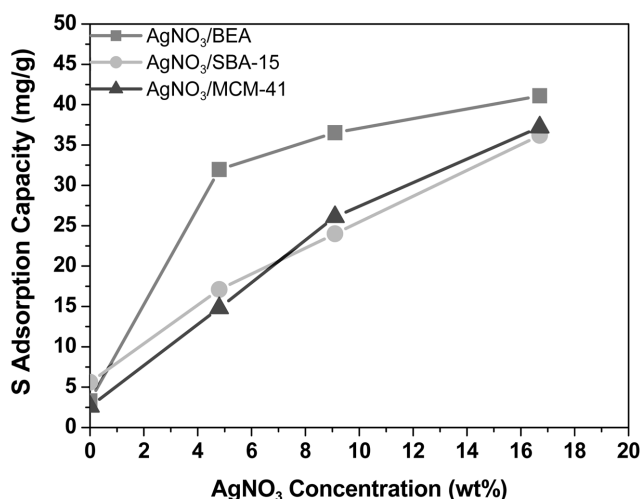


Fig. 3. The change of sulfur adsorption capacities depending on the concentration of  $\text{AgNO}_3$  and sorts of substrates: (■)  $\text{AgNO}_3/\text{BEA}$ , (●)  $\text{AgNO}_3/\text{SBA-15}$ , (▲)  $\text{AgNO}_3/\text{MCM-41}$ .

Table 1. Surface area and pore volume of each substrate obtained by  $\text{N}_2$  adsorption at 77 K

Substrate	Surface area ( $\text{m}^2/\text{g}$ )	Pore volume ( $\text{cm}^3/\text{g}$ )
H-BEA	556	0.355
MCM-41	720	0.950
SBA-15	671	1.080

ruptly at certain points. These points, where sulfur concentration of effluent gas reached 0.1 ppmv, were defined as breakthrough points, and sulfur adsorption capacities were calculated based on these points.

Fig. 3 displays the change of sulfur adsorption capacity depending on the concentration of  $\text{AgNO}_3$  and sorts of substrates. The sulfur adsorption capacities of pristine substrates, such as H-BEA, MCM-41, SBA-15 were very low, in spite of their high surface areas (more than  $550 \text{ m}^2/\text{g}$ ), as shown in Table 1. For all samples, the increase of  $\text{AgNO}_3$  concentration enhanced the sulfur adsorption capacity. It indicates that  $\text{AgNO}_3$ , impregnated on substrates, plays an important role in sulfur compounds adsorption. The highest adsorption capacity among adsorbents prepared in this experiment, 41.1

mg S per one gram of adsorbent (mg/g) by 16.7 wt%  $\text{AgNO}_3/\text{BEA}$ , was comparable to the reported highest value (42.4 mg/g) using silver ion exchanged Y zeolite as adsorbent [8,9].

Although the surface area and pore volume of H-BEA are smaller than those of MCM-41 or SBA-15, sulfur adsorption capacity of  $\text{AgNO}_3/\text{BEA}$  is higher than that of  $\text{AgNO}_3/\text{MCM-41}$  or  $\text{AgNO}_3/\text{SBA-15}$  in all the range of  $\text{AgNO}_3$  concentration shown in this experiment. At low  $\text{AgNO}_3$  concentration of 4.8 wt,  $\text{AgNO}_3/\text{BEA}$  shows much higher sulfur adsorption capacity than that of  $\text{AgNO}_3/\text{MCM-41}$  or  $\text{AgNO}_3/\text{SBA-15}$ . It mainly comes from the chemical environment of the  $\text{AgNO}_3$  located inside the substrates. On mesoporous silica substrates, such as MCM-41 and SBA-15,  $\text{AgNO}_3$  is dispersed as small size crystallites. So, sulfur adsorption capacity is linearly dependent on  $\text{AgNO}_3$  concentration. On the other hand, BEA has ion exchange sites ( $\text{Si}/\text{Al}=50$ ). Thus, some portion of  $\text{AgNO}_3$  molecules are initially distributed on BEA as  $\text{Ag}^+$  ion on  $\text{H}^+$  sites at lower  $\text{AgNO}_3$  concentration. As the concentration of  $\text{AgNO}_3$  increases, however, ion exchange sites are fully occupied by  $\text{Ag}^+$  and excess amount of  $\text{AgNO}_3$  dispersed on BEA as crystallites. So the sulfur adsorption capacity is not linearly dependent on the concentration of  $\text{AgNO}_3$ . Based on these results, H-BEA seems to be a better substrate to accommodate  $\text{AgNO}_3$  for the sulfur adsorption than MCM-41 and SBA-15, especially at low concentration.

Fig. 4 shows the relationship between Sulfur/ $\text{AgNO}_3$  (number of sulfur molecules per one  $\text{AgNO}_3$ ) and  $\text{AgNO}_3$  concentration depending on the substrates. For all the adsorbents, the increase of  $\text{AgNO}_3$  concentration decreases Sulfur/ $\text{AgNO}_3$ . 4.8 wt%  $\text{AgNO}_3/\text{BEA}$  shows the highest Sulfur/ $\text{AgNO}_3$  of 3.54, among all the adsorbents. Although the  $\text{AgNO}_3$  concentration of adsorbent increases to 16.9 wt%, Sulfur/ $\text{AgNO}_3$  is even higher than 1. In previous studies, sulfur compounds adsorptions on various types of adsorbents were mainly explained by chemisorption, because sulfur adsorption capacity was related with number and strength of acid sites or ion exchange ratio of  $\text{Ag}^+$  inside Y zeolite [7-9]. If chemisorption is the only adsorption mechanism, the Sulfur/ $\text{AgNO}_3$  of  $\text{AgNO}_3/\text{BEA}$  should not ex-

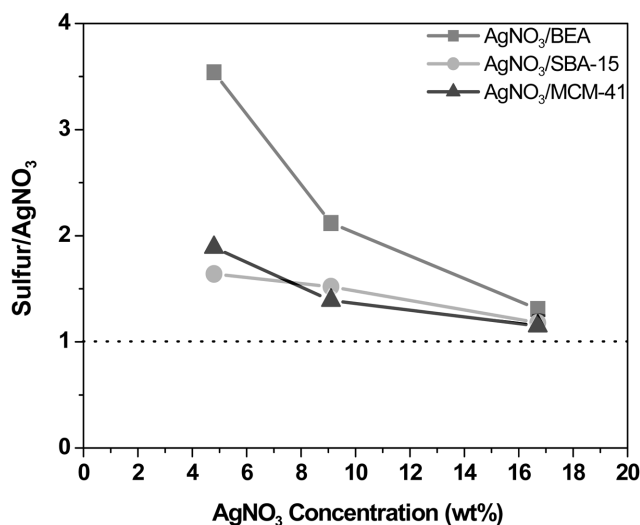


Fig. 4. The change of molar ratio between sulfur per  $\text{AgNO}_3$  (Sulfur/ $\text{AgNO}_3$ ) according to the  $\text{AgNO}_3$  concentration and kinds of substrates: (■)  $\text{AgNO}_3/\text{BEA}$ , (●)  $\text{AgNO}_3/\text{SBA-15}$ , (▲)  $\text{AgNO}_3/\text{MCM-41}$ .

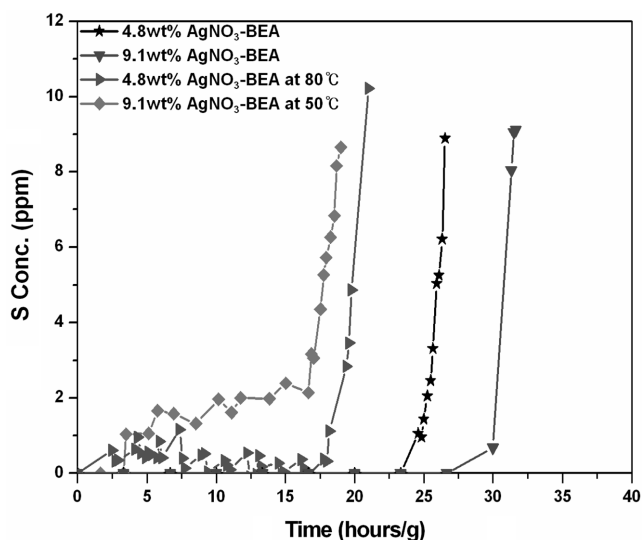


Fig. 5. The change of breakthrough curves for simulated city-gas depending on the adsorption temperature (The weight of each sample was fixed for 0.3 g): (★) 4.8 wt%  $\text{AgNO}_3/\text{BEA}$  at 25 °C, (▼) 9.1 wt%  $\text{AgNO}_3/\text{BEA}$  at 25 °C, (▴) 4.8 wt%  $\text{AgNO}_3/\text{BEA}$  at 80 °C, (◆) 9.1 wt%  $\text{AgNO}_3/\text{BEA}$  at 50 °C.

ceed 0.5, because the stable reaction product between Ag and S is  $\text{Ag}_2\text{S}$ . But, Fig. 4 shows that Sulfur/ $\text{AgNO}_3$  of all adsorbents has higher than 1. Unexpected high values of Sulfur/ $\text{AgNO}_3$  suggests that multi-layer adsorption on  $\text{AgNO}_3$  occurred.

In order to get further insight on the adsorption mechanism of  $\text{AgNO}_3/\text{BEA}$ , breakthrough curves for  $\text{AgNO}_3/\text{BEA}$  with different  $\text{AgNO}_3$  concentration were obtained depending on the adsorption temperature. As shown in Fig. 5, when 4.8 wt%  $\text{AgNO}_3/\text{BEA}$  was used as adsorbent, the increase of adsorption temperature from 25 °C to 80 °C reduced sulfur adsorption capacity by 28%. In case of 9.1 wt%  $\text{AgNO}_3/\text{BEA}$ , smaller temperature increase from 25 °C to 50 °C reduced sulfur adsorption capacity by 28%. In addition to breakthrough time, the increase of adsorption temperature changed the shape of breakthrough curves. The breakthrough curve of 9.1 wt%  $\text{AgNO}_3/\text{BEA}$  at 25 °C indicates that most of the sulfur compounds in city-gas were completely removed by the adsorbent before the breakthrough time. However, the sulfur compounds affinity of adsorbent decreased at 50 °C so that a small portion of sulfur compounds already passed through the adsorbent before the breakthrough time. It means that the bonding between adsorbent and sulfur compound became relatively weak even with small temperature increase. If the adsorption of sulfur compound on the adsorbent is mainly governed by chemisorption, which originates from the strong interaction between sulfur compounds and acid sites or  $\text{Ag}^+$  ion, the sulfur adsorption capacity would not be affected by that much. Based on these experimental results, physisorption appears to be involved in the sulfur compounds adsorption mechanism in addition to chemisorption.

## CONCLUSIONS

Silver nitrate impregnated on substrates, such as beta zeolite, mesoporous silica MCM-41, and SBA-15 was used as adsorbent to re-

move sulfur compounds in city-gas. The sulfur adsorption capacities of  $\text{AgNO}_3/\text{BEA}$ ,  $\text{AgNO}_3/\text{MCM-41}$  and  $\text{AgNO}_3/\text{SBA-15}$  increased as the concentration of  $\text{AgNO}_3$  increased. Among these adsorbents,  $\text{AgNO}_3/\text{BEA}$  showed the highest sulfur adsorption capacity. The temperature-dependent sulfur adsorption capacity and unexpected high Sulfur/ $\text{AgNO}_3$  values strongly suggest that the driving force for sulfur compounds adsorption on  $\text{AgNO}_3/\text{BEA}$ ,  $\text{Ag}/\text{MCM-41}$ ,  $\text{Ag}/\text{SBA-15}$  is not only chemisorption but also physisorption.

## REFERENCES

1. P. J. de Wild, R. G. Nyqvist, F. A. Bruijn and E. R. Stobbe, *J. Power Sources*, **159**, 995 (2006).
2. J. Lampert, *J. Power Sources*, **131**, 27 (2004).
3. H. Wakita, Y. Ono, Y. Tachibana and M. Hosaka, US patent, 6,579,347 (2003).
4. R. T. Yang, A. J. Hernandez-Maldonado and F. H. Yang, *Science*, **301**, 70 (2003).
5. Y.-K. Song, K. B. Lee, H.-S. Lee and Y.-W. Rhee, *Korean J. Chem. Eng.*, **17**, 691 (2000).
6. V. M. Bhandari, C. H. Ko, J. G. Park, S.-S. Han, S.-H. Cho and J.-N. Kim, *Chem. Eng. Sci.*, **61**, 2599 (2006).
7. H.-S. Rho, J.-Y. Kim, J.-W. Kim, D.-R. Park, J.-D. Kim and S.-S. Yang, *J. Ind. Eng. Chem.*, **10**, 511 (2004).
8. S. Satokawa, Y. Kobayashi and H. Fujiki, *Appl. Catal. B: Env.*, **56**, 51 (2005).
9. H. Wakita, Y. Tachibana and M. Hosaka, *Micropr. Mesopr. Mater.*, **46**, 237 (2001).
10. R. Ryoo and J. M. Kim, *J. Chem. Soc., Chem. Commun.*, 711 (1995).
11. M. Kruk, M. Jaroniec, C. H. Ko and R. Ryoo, *Chem. Mater.*, **12**, 1961 (2000).