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# Desulfurization using ZnO nanostructure prepared by matrix assisted method

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**Abstract**−A ZnO nanostructure having a high surface area was developed for use as a desulfurization sorbent. The ZnO nanostructure was prepared by using zinc acetate and activated carbon by the matrix-assisted method. Activated carbon was the matrix in the matrix-assisted method and zinc acetate was the precursor. The desulfurization tests of the ZnO nanostructure were carried out in a packed bed desulfurization system in the temperature range of 300-500 °C. The ZnO nanostructures before and after the sulfidation process were characterized by BET, XRD and SEM. The formulated ZnO nanostructure consisted of ZnO nanoparticles with a size of 10-20 nm and its surface area was very high. Therefore, the sulfur capture efficiency of the ZnO nanostructure was 3 times higher than that of commercial ZnO. However, a reduction of some of the ZnO occurred because of the reducibility of the coal-derived gas, and the surface area of the ZnO nanostructure was slightly reduced due to the sintering of ZnO. It was also confirmed that the silica and alumina containing activated carbon used as the matrix prevent the thermal sintering of ZnO in the sulfidation process at high temperature.

Key words: ZnO Nanostructure, Ultra Cleanup Coal Gas, Matrix-assisted Method, Activated Carbon

## INTRODUCTION

Zinc oxide is an excellent candidate for electro and electro-optical devices, such as piezoelectric devices, transparent electrodes, blue-violet optical emission devices and catalysts. The size and shape of ZnO nanoparticles depend on the method of preparation, which can be chemical vapor deposition (CVD), electro-deposition, vapor phase transport, thermal evaporation using ZnO powder, etc. [1-7]. Herein, nano-sized ZnO was synthesized by the matrix-assisted method, and its possible application to the hot gas desulfurization (HGD) process in integrated gasification combined cycle (IGCC) power plants was studied. The sorbents used for ultra gas cleaning in the HGD process are required to have not only a fast reaction rate in a gas-solid phase reaction, but also a high sulfur capacity in order to reduce the low concentration of sulfur compounds ($H_2S$) contained in the gasified fuel gas from 50 ppmv to 60 ppbv. These sorbents should have a high surface area to meet this requirement.

The matrix-assisted method is a new technique designed to increase the surface area of metal oxides without any loss of the precursors. In the matrix-assisted method, materials having a large surface area such as activated carbon are used as the matrix and precursors to formulate a metal oxide loaded on their surface. The metal oxide with a high surface area is obtained by the removal of the spent activated carbon under an oxidizing atmosphere at high temperature [8]. We formulated zinc oxide having a high surface area by the matrix-assisted method with a zinc-based precursor. The desulfurization properties of the high surface area ZnO nanostructure prepared by the matrix-assisted method were investigated in the hot gas desulfurization process. The physical properties of the ZnO nanostructure, such as its surface area, structure and surface morphology, were measured by BET, XRD, SEM and TEM. The desulfurization tests for the ZnO nanostructure were performed in a fixed-bed reactor.

## EXPERIMENTAL

### 1. Synthesis of ZnO by Matrix-assisted Method

The metal oxide sorbents with a high surface area used for the HGD process were prepared by the matrix-assisted method [9] in order to reduce the amount of sulfur compound ($H_2S$) in gasified fuel gas to less than 50 ppbv. In the preparation of the metal oxide sorbents having a high surface area, a granular type of activated carbon (Aldrich Co.) was used as the matrix, and the metal oxide was supported by the impregnation method. Zinc acetate ($Zn(C_2H_3O_2)_2$ $2H_2O$, Aldrich Co.) was used as the precursor to formulate the metal oxide. The prepared precursor/activated carbon sorbents were dried for 12 hours at 150 °C to remove any moisture from the material. The dried sorbent was then calcined for 6 hours at 550 °C. The surface area, structure and surface morphology of the prepared ZnO sorbent were measured with Brunauer-Emmett-Teller (BET) surface area measurements (QuantaChrom, Autosorb-1-C), X-ray diffraction (XRD; Rigaku D/MAX-2500), scanning electron microscopy (SEM; Hitachi S-4100), electron dispersive X-ray spectrometry (EDX; Horiba EX-300) and transmission electron microscopy (TEM; Hitachi H-7600).

### 2. Desulfurization Tests for Nano Size ZnO

Sulfidation was performed in a vertical type fixed-bed reactor with a diameter of 10 mm placed in an electric furnace. A detailed description of the experimental setup is given elsewhere [10]. The experimental conditions and the compositions of the simulated coal gases are shown in Table 1. The flow rates of the simulated coal

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**Table 1. Experimental conditions and compositions of simulated coal gas**

| Experimental conditions | $N_2$-balance conditions | Simulated coal gas conditions |
|---|---|---|
| Sulfidation temperatures, °C | 300, 400, 500 | 300, 400, 500 |
| Space velocity, ml/h g-sorbent | 30000 | 30000 |
| Pressure, mmHg | 760 | 760 |
| $H_2S$, ppmv | 25 | 25 |
| CO, vol% | - | 17.2 |
| $H_2$, vol% | - | 10.6 |
| $CO_2$, vol% | - | 6.1 |
| $H_2O$, vol% | - | 10 |
| $N_2$, vol% | Balance | Balance |

gas entering the reactor were set to 125 ml/min and controlled by mass flow controllers. All of the volumetric flows of the gases were measured under standard temperature and pressure (STP) conditions. The amount of fresh sorbents in the fixed-bed reactor was 0.25 g. The sulfidation for the ultra cleanup was carried out in the temperature range of 300-500 °C. The outlet gases from the reactor were automatically analyzed by a gas chromatograph (GC, Donam instrument 2400A) equipped with a thermal conductivity detector (TCD) and a pulsed flammable photometric detector (PFPD, OI instrument Co.). The columns used in the analysis were a 1/8 inch Teflon tube packed with Chromosil-310 (Supalco) and a GS-GASPRO capillary tube. The detectability of $H_2S$ with the PFPD used in this study was 10 ppbv. The two kinds of gases used in this experiment were $N_2$ balance and simulated coal gas, each containing 25 ppmv $H_2S$. When the $H_2S$ concentration of the outlet gases reached 2 ppmv, the inlet stream was stopped. The sulfur capacity for the prepared ZnO was also calculated from the $H_2S$ breakthrough time.

## RESULTS AND DISCUSSION

### 1. Morphologies of ZnO Nanostructure

The ZnO nanostructure having a high surface area used for coal gas ultra cleanup was prepared by the matrix-assisted method. It was reported in a previous study that the surface morphologies of ZnO nanostructures varied according to the kind of precursor material used for their synthesis [11]. In this study, zinc acetate was used as the precursor for the synthesis of the ZnO nanostructure having a high surface area. It was confirmed by SEM that the ZnO nanostructure synthesized with zinc acetate consisted of nanoparticles with a size of about 10-20 nm, as shown in Fig. 1. The morphology of the ZnO nanostructure was also investigated by TEM. According to the TEM observations, the ZnO nanostructure prepared with zinc acetate was composed of particles with a spherical type whose size was about 10-20 nm and was uniform, as shown in Fig. 2. The sorbent used for the ultra cleanup of coal gas should have a high surface area. The surface area of the metal oxide significantly affects the reaction rate in the gas and solid reaction system. In particular, the gas absorption and adsorption rates for the absorption and adsorption processes increased as the surface area of the material increased. Therefore, these materials, which were formulated by the matrix-assisted method, were excellent sorbents for the ultra cleanup of coal gas containing hydrogen sulfide.

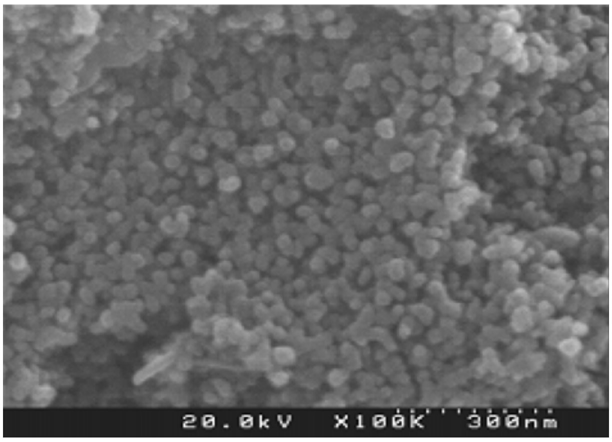

**Fig. 1. SEM image of ZnO nanostructure synthesized by matrix-assisted method.**

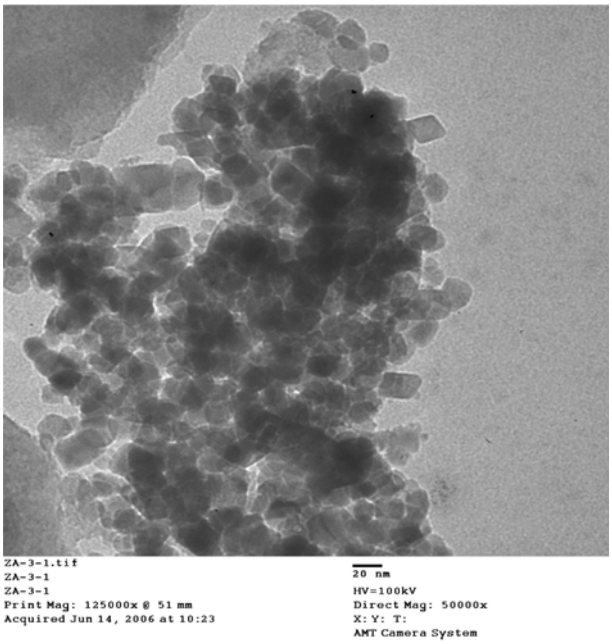

**Fig. 2. TEM image of ZnO nanostructure synthesized by matrix-assisted method.**

### 2. Physical and Chemical Properties of ZnO Nanostructure

The physical and chemical properties of the ZnO nanostructure synthesized for the ultra cleanup of coal gas were investigated by BET, EDX and XRD. The surface area of the ZnO nanostructure, which was synthesized by the matrix-assisted method, was about 23.5 $m^2/g$, which is about 3 times higher than that of commercial ZnO powder (4.49 $m^2/g$). The crystal structure of the ZnO nanostructure synthesized by the matrix-assisted method was analyzed by XRD. The XRD pattern of the ZnO nanostructure matched the typical peak pattern of the ZnO wurtzite structure, as shown in Fig. 3(a). The XRD pattern of ZnO showed an intensity ratio of 50 : 30 : 100 for the peaks at 2 theta=31°, 33° and 36°, respectively.

The other XRD peaks with a high intensity were observed at 2 theta=21 and 26.8°, as shown in Fig. 3(a). It was concluded that

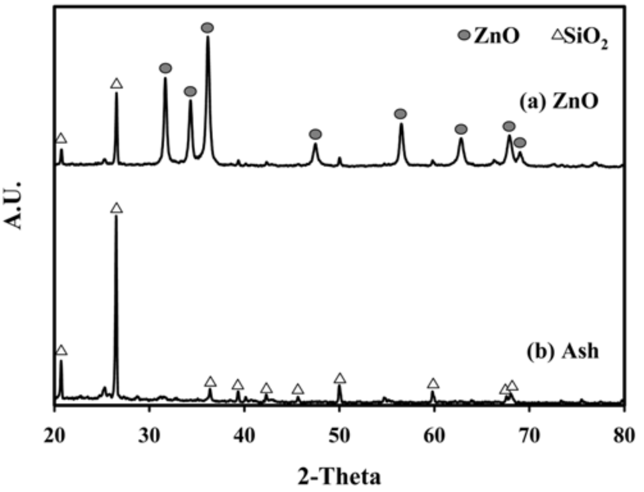

**Fig. 3. XRD patterns of (a) ZnO nanostructure synthesized by matrix-assisted method and (b) ash obtained from calcination of activated carbon used as the matrix material at 550 °C.**

these XRD peaks corresponded to the Si species. It has been reported that the activated carbon used as the matrix material contains carbon and small amounts of several mineral components, such as silica and alumina. Therefore, the activated carbon used in this study was calcined in a furnace at 550 °C, and the elements present in the ash obtained were analyzed by EDX. Silicon, aluminum and oxygen were detected as the elements present in the ash, as shown Fig. 4(a) and the weight contents of these components were 27.62% (Si), 10.38% (Al) and 62.00% (O), respectively. The ZnO nanostructure synthesized by the matrix-assisted method was analyzed by EDX and about 13.62% of silicon was detected. However, no aluminum was detected in the ZnO nanostructure. We concluded that the small amount of aluminum contained in the ZnO nanostructure was not detected due to the ZnO coated on the surface of the matrix. It was also confirmed by comparison with the JCPDS card that the peaks at the 2 theta (intensity ratio) values of 20.9° (21.2), 26.6° (100), 50.1° (11.1) in the XRD pattern, as shown in Figs. 3(a) and (b), agreed with those of $SiO_2$ with a hexagonal structure. No peaks corresponding to any Al species were observed in the XRD pattern because of the presence of amorphous aluminum oxide. It was reported that inert additives such as alumina and silica can prevent the sintering of zinc-based sorbents under high temperature conditions [12-14]. We concluded that the silica and alumina contained in the ZnO nanostructure formulated by the matrix-assisted method would prevent the sintering of the ZnO nanoparticles at high temperature. The sintering of the ZnO nanoparticles caused a reduction in the surface area. Therefore, we expected that the ZnO nanostructure prepared by the matrix-assisted method would be stable under high temperature conditions, due to the prevention of ZnO sintering by the silica and alumina contained within it.

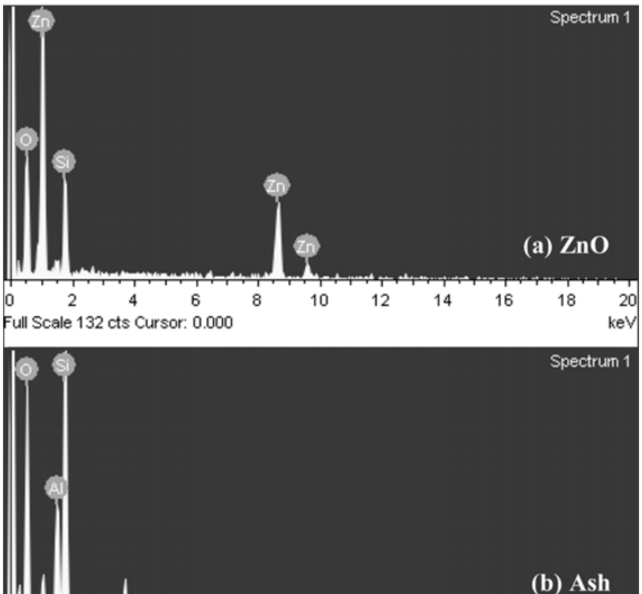

**Fig. 4. EDX diagram of (a) ZnO nanostructure synthesized by matrix-assisted method and (b) ash obtained from calcination of activated carbon used as the matrix material at 550 °C.**

### 3. Desulfurization Tests for ZnO Nanostructure Under Simulated Coal Gas

The ability of the ZnO nanostructure to act as a sorbent for hot gas desulfurization in a fixed bed gas-solid reaction system was studied. The $H_2S$ absorption test of the ZnO nanostructure formulated by the matrix-assisted method was carried out in comparison with that of commercial ZnO powder used for the ultra cleanup of coal, and the $H_2S$ breakthrough curves obtained as a result of these two experiments are shown in Fig. 5. The conditions used for the desulfurization test are shown in Table 1. The $H_2S$ breakthrough times for the ZnO nanostructure and commercial ZnO were 16.6 h and 5.2 h at a sulfidation temperature of 500 °C, respectively. No $H_2S$ was detected in the outlet of the reactor before the breakthrough time. The sulfur capacities for the ZnO nanostructure and commercial ZnO at the breakthrough time were 1.58 gS/100 g-sorbent and 0.496 gS/100 g-sorbent, respectively. The sulfur capacity of the ZnO nanostructure was higher than that of the commercial ZnO, due to the high surface area of the ZnO nanostructure synthesized by the

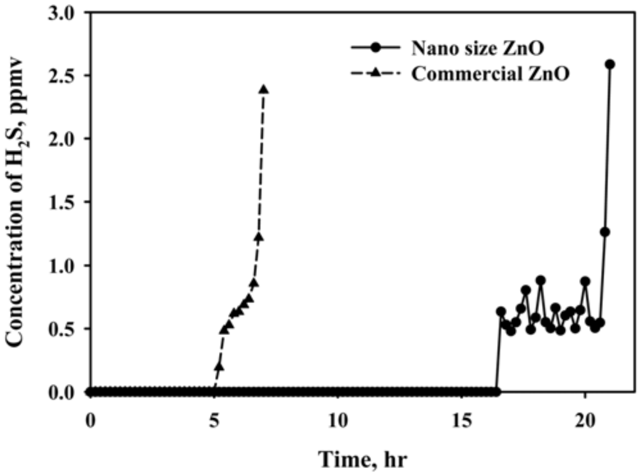

**Fig. 5. $H_2S$ breakthrough curves for commercial ZnO and ZnO nanostructure formulated by matrix-assisted method obtained from the sulfidation tests at 500 °C.**

matrix-assisted method. The surface area of ZnO in the gas-solid reaction system determines the number of absorption sites providing contact between $H_2S$ and ZnO. Therefore, using a ZnO nanostructure having a high surface area is profitable for the ultra cleanup of gas with a low $H_2S$ concentration ranging from less than 25 ppmv to below 60 ppbv. It was reported in our previous study that a high surface area absorbent has a high sulfur absorption rate [8].

## 4. Effect of Reducing Gases

The sulfur absorption behavior of the ZnO nanostructure formulated by the matrix-assisted method was investigated under highly reducing gas conditions using coal derived gas. The typical components of the reducing gas contained in the coal derived gas are hydrogen and carbon monoxide, and the composition of these reducing gases was about 10.6% ($H_2$) and 17.2% (CO). Some of the ZnO is reduced to elemental zinc by the reducing gases under high temperature conditions. Zinc-based sorbents reduced by reducing gases are also easily sintered or melted at a high sulfidation temperature, because the melting point of metallic zinc is 419 °C, and its surface area may be reduced due to the growth of ZnO crystallites resulting from the sintering of the elemental zinc produced by the reduction of ZnO. The reducing gases can be converted to COS and $H_2S$ by their reaction with the ZnS resulting from the sulfidation of ZnO. These reaction behaviors of the reducing gases would deteriorate the sulfur capacity and the sulfur absorption rate of the sorbents.

The sulfidation tests for the ZnO nanostructure synthesized by the matrix-assisted method were carried out under both reducing gas and nitrogen gas balance conditions at sulfidation temperatures of 300 °C, 400 °C and 500 °C; the $H_2S$ breakthrough curves obtained from these experiments are shown in Fig. 6. The $H_2S$ breakthrough time increased with increasing sulfidation temperature, as shown in Fig. 6. This is because of the equilibrium sulfur removal ($ZnO\rightarrow ZnS$). The sulfidation process for $H_2S$ absorption is an exothermic reaction. However, the equilibrium sulfur removal is nearly 100% between room temperature and 800 °C, and decreases above 800 °C [15]. The $H_2S$ absorption rate was also increased, due to the increase of the reaction rate constant as a function of the reaction temperature. Therefore, the $H_2S$ breakthrough time would be expected to increase as the sulfidation temperature increases between room temperature and 800 °C.

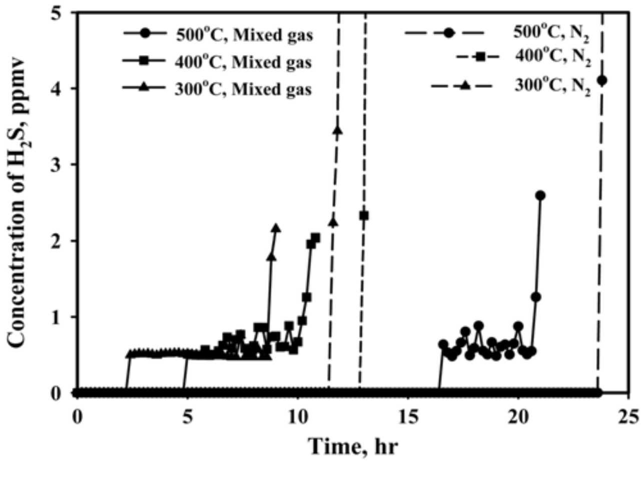

**Fig. 6. $H_2S$ breakthrough curves for ZnO nanostructure obtained from the sulfidation tests under both $N_2$-balance and simulated coal gas conditions at 300, 400 and 500 °C.**

The trends of the $H_2S$ breakthrough curves were different under the reducing gas and $N_2$-balance conditions. The $H_2S$ breakthrough time and sulfur capacity obtained under the reducing gas condition were less than those under the $N_2$-balance condition. No $H_2S$ was detected in the outlet of the reactor before the $H_2S$ breakthrough time when the sulfidation process was carried out under the $N_2$-balance condition. When the same experiment was performed under the reducing gas condition, however, $H_2S$ was detected in the outlet of the reactor at a concentration of about 500 ppbv for 5 h before the $H_2S$ breakthrough time. The trend of the $H_2S$ breakthrough curves obtained at three different reaction temperatures for the sulfidation of the ZnO nanostructure was similar to that observed under the reducing gas condition. It was concluded that $H_2S$ gas was present at a concentration of a few ppmv in the outlet of the reactor due to the deterioration of the ZnO nanostructure by the reducing gases. Therefore, the surface areas of the ZnO nanostructure after the sulfidation process at 300 °C, 400 °C and 500 °C were measured by BET and found to be approximately 18.5 $m^2/g$, 15.9 $m^2/g$ and 17.2 $m^2/g$, respectively. It was confirmed that the efficiency of the ZnO nanostructure for the ultra cleanup of coal gas was lowered, due to the reduction of its surface area by the reducing gases. However, the temperature did not have any significant effect on the surface area. This was attributed to the prevention of the ZnO sintering. No other sulfur species, such as, COS and $SO_2$, were detected.

# CONCLUSION

A ZnO nanostructure for the ultra cleanup of coal gas was formulated by the matrix-assisted method and its physical and chemical properties were analyzed by SEM/EDX, TEM, XRD and BET. The ZnO nanostructure consisted of ZnO nanoparticles with a size of 10-20 nm and had a high surface area. Therefore, the sulfur capture efficiency of the ZnO nanostructure was 3 times higher than that of commercial ZnO. It was also confirmed that the silica and alumina contained in the activated carbon used as the matrix prevented the thermal sintering of ZnO in the sulfidation process at high temperature. However, a reduction of some of the ZnO occurred because of the reducibility of the coal derived gas, and the surface area of the ZnO nanostructure was slightly reduced due to the sintering of ZnO. The sulfur capture efficiency of the ZnO nanostructure was somewhat reduced due to the decrease in its surface area. However, the ZnO nanostructure showed excellent performance for the removal of $H_2S$. It was confirmed that the nano size and high surface area of ZnO formulated by the matrix-assisted method in this study made it effective for the ultra hot gas cleaning of gasified fuel gas.

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# REFERENCES

1. K. Yamamoto, *Physica E*, **24**, 129 (2004).

2. J. Q. Hu, Q. Li, N. B. Wong and C. S. Lee, *Chem. Mater.*, **14**, 1216 (2002).
3. H. Saitoh, M. Saitoh, N. Tanaka, Y. Ueda and S. Ohshio, *Jpn. J. Appl. Phys.*, **38**, 6873 (1999).
4. Y. C. Kong, D. P. Yu, B. Zhang, W. Fang and S. Q. Feng, *Appl. Phys. Lett.*, **78**, 407 (2001).
5. D. Banerjee, J. Y. Lao, D. Z. Wang, J. Y. Huang, Z. F. Ren, D. Steeves, B. Kimball and M. Sennett, *Appl. Phys. Lett.*, **83**, 2061 (2003).
6. J. Lee, K. Park, M. Kang, I. Park, S. Kim, W. K. Cho, H. S. Han and S. Kim, *J. Crystal Growth*, **254**, 423 (2003).
7. Z. W. Pan, Z. R. Dai and Z. L. Wang, *Science*, **291**, 1947 (2001).
8. N. K. Park, J. D. Lee, T. J. Lee, S. O. Ryu and C. H. Chang, *Fuel*, **84**, 2165 (2005).
9. M. Schwickardi, T. Johann, W. Schmidt, O. Busch and F. Schuth, *Stud. Surf. Sci. Catal.*, **143**, 93 (2002).
10. S. O. Ryu, N. K. Park, C. H. Chang, J. C. Kim and T. J. Lee, *Ind. Eng. Chem. Res.*, **43**, 1466 (2004).
11. Y. J. Lee, N.-K. Park, G. B. Han, S. O. Ryu, T. J. Lee and C. H. Chang, *Current Applied Physics*, **8**, 746 (2008).
12. N.-K. Park, Y.-K. Jung, J. D. Lee, T. J. Lee and J. C. Kim, *HWAHAK KONGHAK*, **41**, 667 (2003).
13. N.-K. Park, Y. H. Jung, J. D. Lee, S. O. Ryu and T. J. Lee, *Energy Engg. J.*, **12**, 302 (2003).
14. N.-K. Park, C. U. Lee, S. O. Ryu, T. J. Lee and J. C. Kim, *Energy Engg. J.*, **11**, 136 (2002).
15. P. R. Westmoreland and D. P. Harrison, *Env. Sci. Tech.*, **10**, 659 (1976).