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Effect of H_2SO_4 concentration in washing solution on regeneration of commercial selective catalytic reduction catalyst

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Abstract−Commercial SCR catalysts used in a coal-fired power plant were regenerated by H_2SO_4 solution. The characterization study of the catalysts was carried out by using various analytical techniques. Major deactivating elements for the SCR catalyst were determined and the optimal condition for regeneration of the catalyst was investigated. The catalyst regenerated with 0.5 wt% H_2SO_4 solution showed a high catalytic activity due to an increase in the polymeric vanadates and acid sites by surface sulfates. A higher H_2SO_4 concentration than 2.5 wt% in the washing solution leads to a loss of active components out of the catalyst by dissolution and a dramatic decrease in the surface area.

Key words: SCR Catalyst, Catalyst Deactivation, Regeneration, Coal-fired Power Plant, H_2SO_4 Solution

INTRODUCTION

The selective catalytic reduction (SCR) of nitric oxides with ammonia as reductant is one of the best-proven and world-wide used methods for the removal of NO_X from stationary sources due to its efficiency, selectivity and economics [1-4]. European and Japanese utilities have been installing the SCR units to curb their NO_X emissions since the 1980s [5]. Korea has also installed the De-NO_X process to prevent the evolution of NO_X from the coal, oil and Orimulsion power plants since the late 1990s. V_2O_5-WO_3 as an active catalyst and TiO_2 as a high surface area support are main components of a commercial catalyst for the SCR unit. The catalyst activity is related to the ammonia adsorbed on Brønsted acid sites associated with V^{5+}-OH, while WO_3 increases the number of acid sites and stability of the Brønsted acidity in the catalyst [6]. Such a catalyst is essentially deactivated by various causes when it is employed for the removal of NO_X from the power plants. It was reported that the SCR catalyst used for power generation has to be replaced to the fresh catalyst in 3 to 5 years depending on the operating conditions [7].

Extensive research work has been performed for better understanding about deactivation of the SCR catalyst [6-11]. Alkali metals such as potassium and sodium have been proposed to accelerate the deactivation of SCR catalysts [10]. Among the alkali metals, potassium is the most important element for the deactivation. The deposition of the alkali metals can decrease both the number and the strength of Brønsted acid sites, which are largely responsible to the NO_X removal efficiency [12]. Also, SCR catalyst plugging comes from the deposition of ammonium sulfates and fly ash [10,13]. Other reasons of the catalyst deactivation may be a loss of surface area for sintering and rutilization of titania after long-term operation at high temperature and poisoning by arsenic in the case of wet bottom boilers [1].

The deactivated SCR catalyst has to be regenerated for reuse when considering process economics and environmental impact of heavy metals contained in the used catalyst. While many publications are available in the research area of deactivation of SCR catalyst, few studies on the regeneration of SCR catalyst have been made until now. Khodayari and Odenbrand [6] reported the regeneration of commercial SCR catalysts applied in bio-fuel plants. They proposed that exposing the catalyst surface to sulfate by SO_2 or H_2SO_4 is a promising way to rejuvenate the initial activity of the catalyst poisoned by potassium, which is the major poisoning element in the bio-fuel plants. Zheng et al. [14] also reported the regeneration methods of SCR catalysts deactivated under biomass combustion.

In this study, regeneration of a commercial SCR catalyst used in a coal-fired power plant has been carried out. Our aim is to investigate the causes of the catalyst deactivation in the coal fired boiler and to provide basic engineering data for the rejuvenation of SCR catalyst. The SCR efficiency over the fresh, the deactivated and the regenerated catalysts has been determined at various operating conditions. Furthermore, SCR catalysts have been characterized by a scanning electron microscope (SEM), a temperature-programmed desorption (TPD) and an X-ray diffractometer. An inductively coupled plasma-atomic emission spectrometer (ICP-AES) was used for elemental analyses of the catalyst and a washing solution.

EXPERIMENTAL

1. Catalyst

The catalyst used in this work was a commercial SCR catalyst aged in a power plant using coal as fuel. The composition of fresh catalyst was 11.6 wt% WO_3/0.47 wt% V_2O_5/TiO_2. The catalyst was deactivated by flue gas emitted from the boiler during about 20,000 h.

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Table 1. The regenerated catalysts and the regeneration methods

Sample	Washing solution	Washing period of time	Drying condition
DW	Distilled water	30 min	100 °C, 2 h
HS-0.005	0.005 wt% H_2SO_4 solution	30 min	100 °C, 2 h
HS-0.05	0.05 wt% H_2SO_4 solution	30 min	100 °C, 2 h
HS-0.5-10	0.5 wt% H_2SO_4 solution	10 min	100 °C, 2 h
HS-0.5-30	0.5 wt% H_2SO_4 solution	30 min	100 °C, 2 h
HS-0.5-60	0.5 wt% H_2SO_4 solution	60 min	100 °C, 2 h
HS-2.5-30	2.5 wt% H_2SO_4 solution	30 min	100 °C, 2 h
HS-2.5-300	2.5 wt% H_2SO_4 solution	300 min	100 °C, 2 h
HS-5.0	5.0 wt% H_2SO_4 solution	30 min	100 °C, 2 h

2. Experimental Procedure

The deactivated catalyst was regenerated by washing with various aqueous solutions such as distilled water and different concentrations of sulfuric acid in an ultrasonic cleaner. The washing time was also controlled as an operating variable for the regeneration. After washing, each sample was separated from the solution and dried at 100 °C. The washing solution was analyzed by ICP-AES for elemental analysis. Table 1 summarizes the code of catalysts with different regeneration condition.

NH_3-TPD was carried out in a fixed-bed quartz reactor. A typical sample mass of 0.1 g and a gas flow rate of 300 mL/min were used for the experiment. The dried catalyst was treated with a 500 ppm NH_3/He atmosphere at room temperature for 1 h. Physically adsorbed NH_3 was removed in N_2 at 100 °C. Desorption of chemisorbed NH_3 was accomplished by heating the sample to 550 °C with a rate of 10 °C/min under N_2 atmosphere, and the concentration of NH_3 was measured by a TC detector. Surface area of the catalyst was measured by the Brunauer-Emmett-Teller (BET) method and the average pore diameter was calculated from the surface area and the BET pore volume by using Micromeritics ASAP 2000. The crystalline structure of catalyst before and after regeneration was analyzed by XRD.

The SCR activity test of catalysts was conducted in a continuous flow reactor, where a catalyst cell of 30 mm×30 mm×45 mm in size was placed inside a furnace. The catalyst activity was measured at a steady state condition. The experimental equipment consisted of three sections: reactor, gas feeding system, and gas analyzer. The SCR catalyst was placed in the reactor and then the catalyst was heated to the desired reaction temperature. When the system reached steady state, the preheated mixed gas (200 ppmv NO/240 ppmv NH_3/500 ppmv SO_2/3 vol% O_2/10 vol% H_2O/N_2 balance) was introduced into the reactor with a space velocity of 20,000 h^{-1}. The concentrations of NO and SO_2 were measured by gas analyzers (Rosemount, 880 A) using a nondispersed infrared (ND-IR) method and the concentration of O_2 was detected with a analyzer with zirconium oxide sensor (Rosemount, OXA 1000).

RESULTS AND DISCUSSION

1. ICP-AES Analysis of the SCR Catalyst

In a commercial operation, the surface of SCR catalyst is deposited by the elements of fly ash discharged from the coal-fired power plant, which leads to the catalyst deactivation. Thus, fly ash was analyzed to determine the major deactivating element for the SCR catalyst, which was installed before an electrostatic precipitator (Table 2). Arsenic, alkali metal (potassium and sodium), and alkali earth metal (calcium) have been known to deactivate the SCR catalyst [1,10,12]. Also, iron, phosphorus and sulfur were detected by the ICP-AES analysis.

Table 3 summarizes ICP-AES analysis results of the SCR catalysts. Deactivated catalyst contains much higher concentration of the poisoning elements such as As, Ca, K, Na and S compared to the fresh catalyst. On the other hand, phosphorus was not detected

Table 2. ICP-AES analysis result of fly ash of the coal-fired power plant

Element	As	Ca	K	Na	Fe	P	S
Content (ppm)	10,324	43,855	11,465	15,773	70,481	2,713	2,965

Table 3. ICP-AES analysis results of fresh, deactivated and regenerated catalysts

Element (ppm)	As	Ca	K	Na	Fe	P	S
Fresh catalyst	58	104	n.d.	176	174	9905	1481
Deactivated catalyst	2441	187	486	603	2173	n.d.	3323
DW	1055	172	45	109	744	n.d.	1037
HS-0.005	1065	130	92	118	1226	n.d.	1173
HS-0.05	1258	85	95	115	1059	n.d.	1128
HS-0.5-30	1151	79	44	197	763	n.d.	1273
HS-2.5-30	1283	83	49	107	1342	n.d.	2012
HS-5.0	1194	78	38	157	Not measured	n.d.	3078

by ICP-AES in the deactivated catalyst, indicating that the phosphorus compounds contained in the fly ash and the fresh catalyst are the oxide phases with low boiling point and high vapor pressure. Arsenic (As) as gaseous As_2O_3 is thought to deactivate the catalyst by blocking micropores of the catalyst and chemical binding to active site provided by vanadium oxide [15].

We have to note that K and Na dramatically increased in the catalyst used commercially. It was reported that the effect of deposition of alkali metals on SCR commercial catalysts surface results in a significant loss of surface acidity [10,14]. Potassium has a stronger neutralizing effect with respect to sodium [10]. Zheng et al. [13] proposed that the Brønsted acid sites are chemically altered by the presence of potassium as follows:

$$\text{-V-OH+K}^+ \rightarrow \text{-V-O-K+H}^+ \quad (1)$$

The surface potassium compound is known to form a complex metal oxide of K_2SO_7-V_2O_5 in the presence of sulfur, which can catalyze the oxidation of SO_2 to SO_3 [10]. Our research group reported that the oxidation of SO_2 is much more active over the deactivated catalyst than the fresh one [7].

Also, the amount of sulfur in the deactivated catalyst increased about 2.5 times higher than that in the fresh catalyst. SO_2 in flue gas can bring about the formation of ammonium sulfates and sulfuric acid as follows:

$$SO_2+1/2O_2 \rightarrow SO_3 \quad (2)$$

$$SO_3+2NH_3+H_2O \rightarrow (NH_4)_2SO_4 \quad (3)$$

$$SO_3+NH_3+H_2O \rightarrow NH_4HSO_4 \quad (4)$$

$$SO_3+H_2O \rightarrow H_2SO_4(g) \quad (5)$$

Fig. 1 shows the Gibbs free energy change as a function of the temperature calculated with HSC chemistry. It can be estimated that ammonium sulfate, $(NH_4)_2SO_4$, can be readily formed at the operating temperature showing a high negative value in the Gibbs free energy change of reaction (3). On the other hand, ammonium bisulfate (NH_4HSO_4) may be hardly formed based on the calculation of Gibbs free energy change. However, those reactions are likely to depend on equilibrium and reaction kinetics. Ammonium sulfates are typical poisoning compounds by deposition on the catalyst surface. H_2SO_4 formation is also feasible once SO_3 is formed by the oxidation of SO_2 catalyzed by vanadium oxide or K_2SO_7-V_2O_5. Gaseous H_2SO_4 might condense to liquid H_2SO_4 in the pore by capillary effect, which leads to retarding of the catalytic activity [16]. Besides those sulfur compounds, metal sulfates could be formed by a reaction between SO_2, O_2 and metal oxide such as TiO_2.

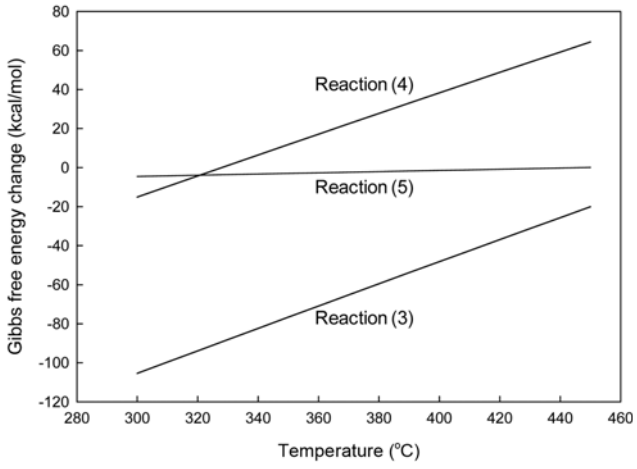

Fig. 1. Gibbs free energy change as a function of temperature calculated by HSC chemistry.

Table 4 summarizes the ICP-AES analysis result of washing solution after regeneration. Poisoning elements (Ca, K, Na, As and P) were detected in the washing solutions, suggesting they are soluble even in low concentration of H_2SO_4 solution. The concentration of the poisoning elements increased when employing a high concentration of 2.5 wt% H_2SO_4 solution (HS-2.5-30) and a longer washing time of 60 min (HS-0.5-60). However, more amounts of V, W and Ti were also dissolved into the washing solution with an increase in the concentration and the washing period. Especially, the concentration of W in the washing solution increased up to 97 ppm after regeneration with 2.5 wt% H_2SO_4 solution. This result implies that a higher concentration of H_2SO_4 in the washing solution leads to a loss of active components out of the catalyst.

2. Image Analysis

Fig. 2 shows the digital images of catalysts discharged from a commercial coal-fired power. Cell plugging of the aged catalyst was found in Fig. 2(A) due to the deposition of fly ash and poisoning materials such as ammonium sulfates. Such a plugging in the cell brings about a decrease in the catalytic activity and an increase in the pressure drop of the SCR facility. After regeneration with a washing solution, most of cell was open as can be seen in Fig. 2(B).

Fig. 3 shows the SEM images of the catalysts before and after

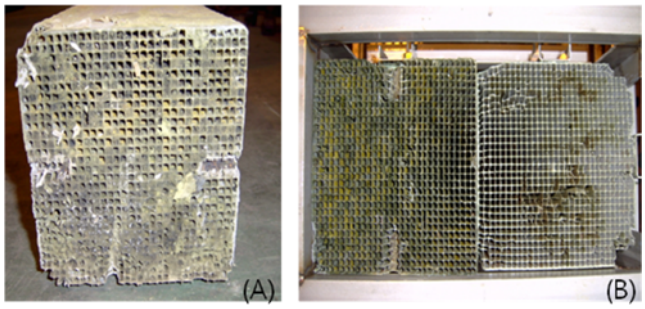

Fig. 2. Photographs of (A) the deactivated commercial catalyst and (B) the regenerated catalyst.

Table 4. ICP-AES analysis result of washing solution after regeneration

Element (ppm)	Ti	V	W	Ca	K	Na	Fe	As	P
HS-0.5-30	1.9	36.4	n.d.	3.2	11.3	16.0	56.2	4.4	1.6
HS-0.5-60	5.0	48.3	13.3	6.6	24.1	24.0	118.5	5.0	2.0
HS-2.5-30	3.0	49.0	96.9	19.0	29.0	50.0	29.0	22.0	11.0

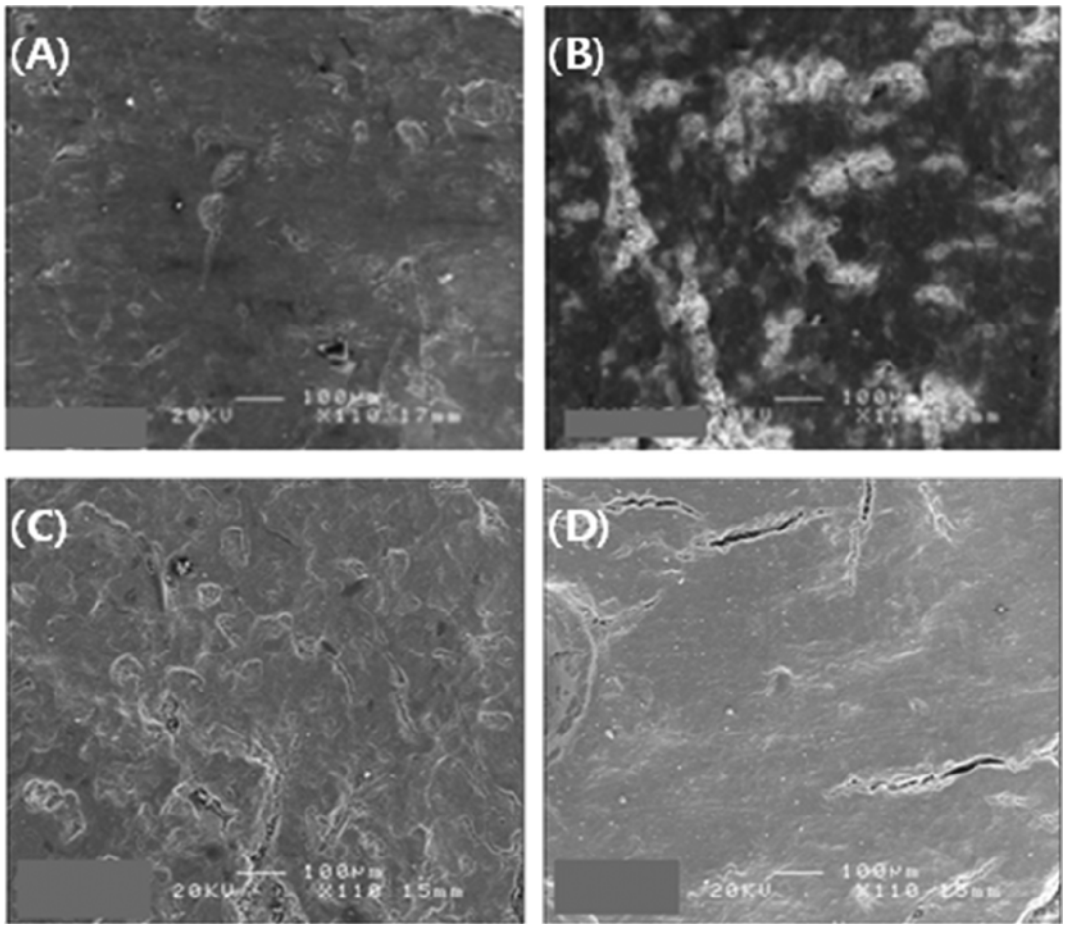

Fig. 3. SEM images of (A) the fresh catalyst, (B) the deactivated catalyst, (C) HS-0.5-30 and (D) HS-2.5-30.

regeneration. As can be seen, the surface of the deactivated catalyst (B) seems to be covered by poisoning materials. According to the EDS analysis, the content of Si, Ca and S on the deactivated catalyst largely increased compared to the fresh catalyst, which was mainly due to the deposition of fly ash and the SO_2 effect described previously. Most of the deposits disappeared after regeneration, and cracks of catalyst surface were also observed when employing a 2.5 wt% H_2SO_4 concentration for the washing solution.

3. Catalytic Activity Test

The catalysts were exposed in a simulated flue gas stream to determine NO_X conversion in the SCR. NO_X conversion was obtained by following equation:

$$NO_X \text{ conversion } (\%) = \left[1 - \frac{[NO]_{outlet}}{[NO]_{inlet}}\right] \times 100 \quad (6)$$

where $[NO]_{inlet}$ and $[NO]_{outlet}$ are the concentration of NO at the reactor inlet and outlet, respectively.

Fig. 4 shows the effect of reaction temperature on NO_X conversion over various catalysts. The deactivated catalyst exhibited the lowest NO_X conversion at a temperature window between 350 and 450 °C because the deactivating elements contained in flue gas brought about the poisoning phenomena by destroying acid sites of the catalyst and by plugging the catalyst pore, etc. The H_2SO_4 effect on the regeneration was noticeable in terms of NO_X conversion. The optimal H_2SO_4 concentration was found to be 0.5 wt% of HS-0.5-30

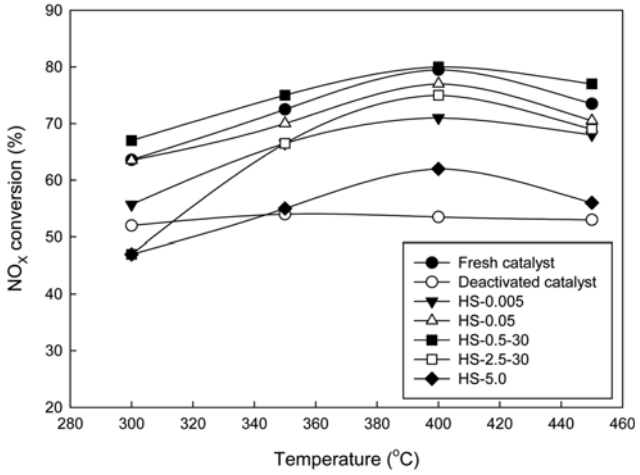

Fig. 4. Effect of reaction temperature on the NO_X conversion over SCR catalysts regenerated by washing solutions with different concentration of H_2SO_4.

catalyst based on NO_X conversion and the catalyst regenerated with a further concentrated solution showed a decline in NO_X conversion. Interestingly, NO_X conversion over HS-0.5-30 is higher than that over the fresh catalyst, indicating an increase in acid sites by sulfate ions [17]. Also, it was reported that surface sulfate species

enhance the formation of the polymeric vanadate, which is known as a major active site, by reducing the available surface area of the catalyst [18]. The catalytic activity of the polymeric vanadate species was suggested to be about 10 times higher than those of the monomeric vanadyl species for SCR reaction [6]. Those sulfate ions were possibly introduced onto the catalyst to form surface sulfates linked to TiO_2 and/or V_2O_5 during the washing step with H_2SO_4 solution. It is believed that the main reason of decrease in NO_X conversion at a higher concentration of H_2SO_4 was dissolution of active component such as V and W in the catalyst. As shown in Table 4, the dissolved amount of V and W to washing solution increased with the H_2SO_4 concentration and the washing period of time. Thus, an excessively high concentration of H_2SO_4 in washing solution has a negative effect on the catalyst regeneration.

Fig. 5 shows the effect of the washing period on NO_X conversion. In case of 0.5 wt% H_2SO_4 solution, washing during 30 min showed the best result in the SCR activity. Low NO_X conversion with a shorter period of time might be due to the remaining deposits on the catalyst surface, while a longer period for washing might lead to a loss of active component by dissolution. Such a washing period effect was prominent when the catalyst was treated with a 2.5 wt% H_2SO_4 solution for 300 min as can be seen in Fig. 5. This result means that the optimal washing period has to be investigated for the regeneration of the SCR catalyst, and in this work the regeneration condition of HS-0.5-30 was found to be suitable to rejuvenate the catalytic activity.

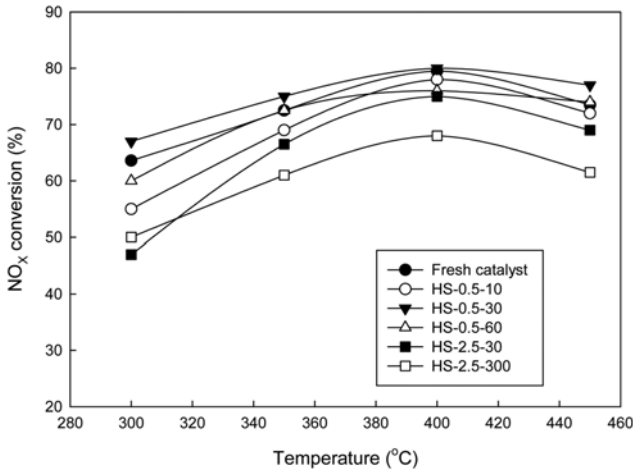

Fig. 5. Effect of reaction temperature on the NO_X conversion over the regenerated catalysts with a variation of the washing period of time.

Table 5. BET surface area, pore volume and average pore diameter

Sample	Surface area (m^2/g)	Pore volume (cc/g)	Average pore diameter (nm)
Fresh catalyst	96	0.220	9.2
Deactivated catalyst	51	0.165	12.6
HS-0.005	69	0.182	10.6
HS-0.05	70	0.188	10.7
HS-0.5-30	75	0.202	10.8
HS-2.5-30	70	0.195	10.9
HS-5	49	0.157	12.5

4. Physical Properties and Crystalline Structure

The BET surface area, the pore volume and the average pore diameter of the catalysts were measured to investigate a change in the physical properties of the catalysts before and after the regeneration. As summarized in Table 5, the surface area and the pore volume of the deactivated catalyst were even lower than those of fresh catalyst. On the other hand, the average pore diameter of the deactivated catalyst was larger than that of the fresh catalyst. This is mainly due to the plugging of the small pore by deposits [19]. The samples regenerated by H_2SO_4 solution showed a tendency of an increase in the surface area and the pore volume when compared with the deactivated catalyst, depending on the concentration of H_2SO_4. This is because most of deposits were removed from the catalyst pore. A pore enlargement of the regenerated catalyst is probably due to the thermal sintering and the residue of deposits remaining in the catalyst even after regeneration because the surface area of regenerated catalyst is smaller than the fresh catalyst. The surface area and the pore volume began to be reduced from HS-2.5-30. Then, they sharply decreased when a 5 wt% H_2SO_4 solution was employed. This result could be explained by the ICP-AES analysis data. The excessively high concentration of H_2SO_4 is likely able to cause dissolution of the metal oxides in the catalyst, which results in larger pore size and lower surface area as can be seen in Table 5. The change in the physical properties and the loss of the active phase could be the main cause for a sharp drop in the catalytic activity of HS-5. Although the HS-0.5-30 catalyst exhibited the best result in Table 5, its physical properties did not reach the level of the fresh catalyst. This result might be evidence that a high catalytic activity of the HS-0.5-30 came from an increase in the polymeric vanadates and the acid sites by surface sulfates, introduced onto the catalyst during regeneration.

Fig. 6 shows the XRD results to determine the crystalline structure of catalysts. Both fresh and deactivated catalysts showed the anatase structure of TiO_2 support, suggesting that the thermal deactivation of the commercial SCR catalyst used in this work was negligible in spite of operation for two years. The regenerated catalysts

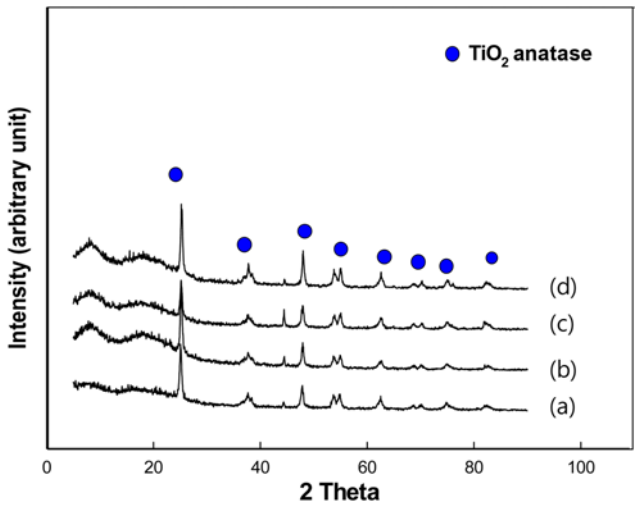

Fig. 6. XRD analysis results of (a) the fresh catalyst, (b) the deactivated catalyst, (c) HS-0.5-30 and (d) HS-2.5-30.

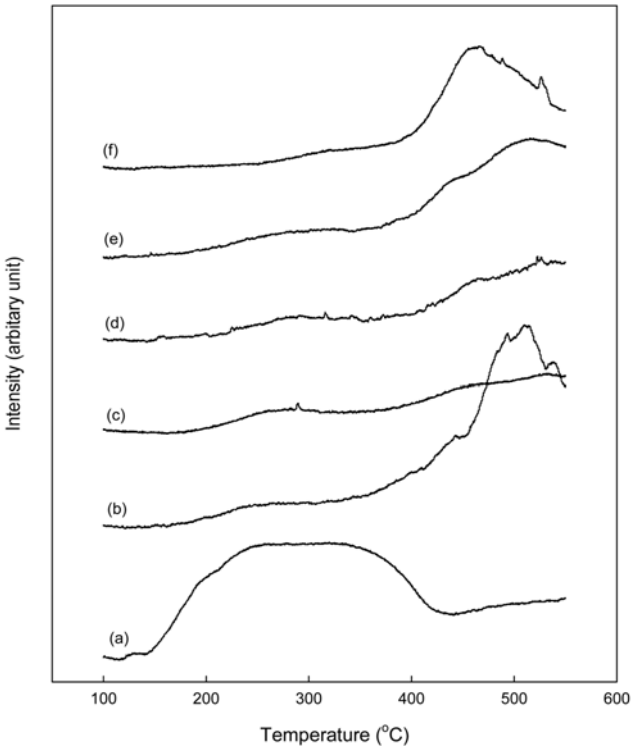

Fig. 7. NH_3-TPD profiles of the catalysts: (a) fresh catalyst, (b) deactivated catalyst, (c) DW, (d) HS-0.5-30, (e) HS-2.5-30 and (f) HS-5.0.

also exhibited the characteristic peaks of anatase. From this result, we can conclude that the concentration of H_2SO_4 less than 2 wt% for a washing solution does not affect the crystalline structure of the catalyst.

5. NH_3-TPD

Fig. 7 shows the NH_3-TPD results of the SCR catalyst. The NH_3 desorption profile of the fresh catalyst showss two unresolved maxima with the peak centers at about 250 and 350 °C. The first peak could be related to NH_3 desorbed from weak Brønsted acid sites, while the second peak could be attributed to the desorption of NH_3 strongly adsorbed on Lewis acid sites [20,21]. As for the deactivated catalyst, desorption intensity of NH_3 was largely diminished by the poisoning and the pore plugging of the catalyst. A sharp peak in NH_3 desorption profile of the deactivated catalyst was found at 500 °C, which might be due to thermal decomposition of the ammonium sulfates deposited on the catalyst surface during the commercial operation. When the catalyst was washed with distilled water, the amount of desorbed NH_3 slightly increased compared with that of the deactivated catalyst and the strong peak disappeared, indicating the deposited ammonium sulfates was successfully removed. When H_2SO_4 solutions were utilized for regenerating the catalyst activity, the NH_3 desorption profile was quite different from that of the fresh catalyst. Smaller amount of NH_3 was desorbed from the regenerated catalyst below 400 °C, while the peak at 500 °C increased gradually with the concentration of H_2SO_4 in the washing solution. Such a peak was probably related to the decomposition of ammonium sulfates, which could be formed by a reaction between the sulfate ions introduced during the washing step and the adsorbed NH_3. It was reported that the SCR catalyst with sulfate contains more Lewis and Brønsted acid sites [4,22]. However, those catalysts were calcined at a high temperature of about 400 °C, while the catalyst treated by the H_2SO_4 solution was only dried at 100 °C in the present work. It can be expected that the sulfates introduced in the present work play an important role in rebuilding the acid sites on the catalyst once it is placed in the SCR unit operated at 350 °C. The sulfate species also might reduce the direct oxidation of NH_3 to N_2 or NO, which results in an increase in the SCR conversion [23]. However, it has to be emphasized that an excessively high concentration of H_2SO_4 could dissolve the components of the catalyst to reduce the SCR activity as described previously.

CONCLUSIONS

Regeneration of a commercial SCR catalyst used in a coal-fired power plant has been carried out in the present study. The deactivated catalyst was regenerated by H_2SO_4 solutions with various concentrations (0.005 to 5 wt%). The poisoning elements of Ca, K, Na, As and S were detected in the deactivated catalyst. Also, a large amount of deposits was observed on the deactivated catalyst. The catalytic activity was recovered by regenerating the catalyst with a H_2SO_4 solution. The optimal H_2SO_4 concentration was found to be 0.5 wt% for the regeneration of commercial catalyst discharged from the power plant. A high catalytic activity over the regenerated catalyst came from an increase in the surface sulfate, which could provide a formation of the polymeric vanadate and acid sites on the catalyst surface. Higher concentration of H_2SO_4 brought about dissolution of active material in the catalyst, which caused a decrease of the SCR efficiency and a loss of surface area. Based on the present experimental result, the pilot plant facility for the regeneration will be constructed and demonstrated for reuse of the commercial SCR catalyst.

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