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The effect of the pore structure of a high surface area hydrated lime in a humid environment

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The degradation behavior of hydrated lime sorbent exposed to a humid environment was investigated in terms of a change of the pore structure, phase transition, and particle aggregation. Di-ethylene glycol (DEG)-coated quicklime was hydrated to prepare a sorbent with a high surface area. The hydrated lime sorbent was maintained in a consistent chamber at 50 °C and 60% relative humidity for 168 h. As the degradation time of the sorbents exposed to the humid environment was increased, the calcite phase fraction was increased due to the carbonation process, whereas the reactivity for SO₂ gas was reduced. A decrease in the specific surface area of the sorbents, from 45.8 m²/g to 7.6 m²/g, was also observed with elapsed degradation time. Also the clogging of small size pores having a size range of 30~40Å was observed due to the particle aggregation and the carbonation process by the humidity. Consequently, the degradation of hydrated lime sorbent in a humid environment was attributed to a collapse of the pore structure originating from the carbonation process and the particle aggregation.

Key words: Hydrated lime sorbent, Humid environment, Pore structure, Particle aggregation, Carbonation process.

Introduction

The in-duct sorbent injection method to remove SO_2 emissions from combustion systems is one of the dry flue gas desulfurization (FGD) processes. During this process, alkaline sorbent particles are introduced into a flue gas in the duct between the air pre-heater and the particulate control device in which the temperature and the humidity are controlled. As for an alkaline sorbent for SO_2 removal, hydrated lime or slaked lime (calcium hydroxide, Ca(OH)₂) is widely used [1].

In order to improve the desulfurization efficiency of the system, hydrated lime sorbent must have a small particle size, a high specific surface area, a high pore volume, and a large pore diameter [2]. The properties of the sorbent such as its specific surface area and porosity take an important role in removing the SO₂. Previous studies have shown that the reaction towards SO₂ gas depends strongly on the specific surface area of the sorbent [3, 4].

Numerous studies have shown how preparation of the sorbent affects the efficiency in removing SO_2 , and modeled the reaction mechanisms [3, 5-9]. However, it is not enough to study the performance decay and the degradation behavior of hydrated lime sorbent. In

general, the as-produced hydrated lime sorbent, in industry, can be preserved in a silo or storage facilities before it is sprayed into dry FGD systems. During this period of storage, the sorbent is exposed to a humid environment and the reactivity for SO₂ gas is decreased. The degraded sorbent cannot be used for SO₂ gas removal or a larger amount of degraded sorbent must be sprayed into the dry FGD system than that of as-produced sorbent. Therefore, a study of the degradation behavior of hydrated lime sorbent in a humid environment is needed to find possible solutions to prolong the efficiency for SO₂ removal and improve the durability.

Previously, we have studied the degradation behavior of hydrated lime sorbent in a humid environment. As for the degraded sorbent in a humid environment, a decrease in the specific surface area with elapsed degradation time was observed and it resulted from the carbonation reaction and the aggregation of the sorbent [10].

In this study, we have investigated the change the of pore structure with respect to a decrease in the specific surface area in the degraded sorbent. The pore structure of the hydrated lime sorbent was examined by nitrogen adsorption-desorption isotherms and pore size distributions. The effects of the carbonation reaction and the aggregation with regard to change of the pore structure have also been discussed.

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Hydrated lime sorbent for SO₂ removal was prepared

using the hydration method. To obtain quicklime, limestone was calcined at 1100 °C for 3 h. Di-ethylene glycol (DEG) as a dispersion agent was added to the quicklime powder and the DEG-coated quicklime was hydrated using distilled water. Then the hydrated lime sorbent was obtained through the reaction between the DEG-coated quicklime and distilled water of 1.8 times the stoichiometric amount. This preparation method for the hydrated lime sorbent with a high specific surface area was described previously [11, 12].

A degradation test of the as-prepared sorbent was progressed under atmospheric pressure using a chamber maintained at a constant temperature of 50 °C and a humidity of 60% relative humidity (RH) for up to 168 h. Such conditions of the degradation tests have been described in our previous publication [10].

The crystal phases of the hydrated lime sorbents were analyzed using an X-ray diffractometer (Bruker, D8 Advance). XRD patterns were recorded in the 2 θ range of 10-60° using Cu K α (1.5406 Å) radiation. The SO₂ reactivity of hydrated lime sorbents was measured using a thermo-gravimetric (TG) analyzer (SHIMADZU, TMA-60H). N₂ gas containing 2,000 ppm SO₂ gas was used as a standard reaction gas to analyze the sulfation reactivity. The flow rate of the gas was 100 ml/minute and the sulfation reaction was held at 350 °C for 4 h.

Specific surface areas and pore structure studies were determined by nitrogen adsorption isotherms measured at 77 K using a N_2 adsorption analyzer (Micromeritics ASAP 2010). The Brunauer, Emmett and Teller (BET) and Barrett, Joyner and Halenda (BJH) models were used to estimate the specific surface area and the pore structure of the sorbents according to the nitrogen adsorption isotherms.

Morphological analysis was performed in a field emission-scanning electron microscope (FE-SEM, Hitachi S-4800) and selected area electron diffraction (SAED) patterns were also observed by a transmission electron microscope (TEM,JEN 2100F).

Results and Discussion

In figure 1, XRD patterns show the phase transition from potlandite to calcite of the hydrated lime sorbents as a function of degradation time. The as-prepared sorbent indicates a complete hydration of quicklime (CaO) into portlandite (Ca(OH)₂). However, the degraded sorbents exposed to the humid environment for 24~168 h showed that the portlandite phase fraction was reduced, whereas the calcite phase fraction was increased because of the carbonation process. In particular, the decrease of the (101) main peak of portlandite and the growth of the (104) main peak of calcite were remarkable. The longer time the hydrated limes were exposed to the humid environment, the less the amount of the portlandite phase and the more the amount of the calcite phase became.



Fig. 1. XRD patterns of hydrated lime sorbents as-prepared (0 h) and degraded which were exposed to a humid environment for up to 168 h.



Fig. 2. Reactivity test toward SO₂ gas of as-prepared sorbent and degraded sorbents.

Figure 2 describes the reactivity test toward SO₂ gas of hydrated lime sorbents from thermo-gravimetric analysis. As seen from Fig. 2, the as-prepared sorbent showed a weight increase to 120 wt% and the degraded sorbents for 48 h and for 168 h showed 113 wt% and 104 wt% increase, respectively. The as-prepared sorbent towards SO₂ gas showed a greater reactivity than the degraded sorbents. The slope obtained from the weight changetime curves can be interpreted as the reactivity of the sorbents. At an initial time of 60 minutes, the slopes were taken and the as-prepared sorbent also exhibited the highest value compared to the other slopes. These results indicate that the hydrated lime sorbents show a degraded SO₂ removal performance when exposed to a humid environment.

In order to verify the relations between the specific

Table 1. The variation in the specific surface area of hydrated lime sorbents as a function of degradation time.



Fig. 3. Nitrogen adsorption and desorption isotherms of hydrated lime sorbents as-prepared and degraded for 48 h and 168 h. The open symbols are adsorption points, the filled symbols are desorption points.

surface area, the pore structure, and its performance decay, the specific surface areas and the pore structure of the hydrated limes were measured as a function of degradation time and recorded in table 1. It was observed that the specific surface area of the asprepared sorbent was larger than that of the sorbent degraded in the humid environment. The as-prepared sorbent shows a specific surface area of $45.7 \text{ m}^2/\text{g}$ and the degraded sorbents for 48 h and 168 h show specific surface areas of $14.6 \text{ m}^2/\text{g}$ and $7.6 \text{ m}^2/\text{g}$, respectively. The BJH (Barret-Joyner-Halenda) method was employed to obtain additional information on the pore shape, the pore volume, and the pore size distribution of the sorbents.

The corresponding adsorption/desorption isotherms of gaseous nitrogen at 77 K are reported in Fig. 3. Isotherms were of type II and reflect the nonporous nature of solids. The largest adsorption volume of nitrogen was observed for the as-prepared sorbent and the adsorption capacity of the sorbents decreased with elapsed degradation time. All of the curves indicate the presence of macropores (size > 50 nm), shown by the sharp rise near P/P₀ values of 1. All isotherms showed a large type H3 hysteresis loop, which did not exhibit any limiting adsorption at high P/P₀. The presence of very large pores, still containing vapor at the end of the adsorption stage of the experiment, results in an adsorption isotherm that is still rising at (P/P₀) max, i.e., an isotherm of type II with an H3 hysteresis loop. This isotherm is "incomplete",



Fig. 4. Pore size distributions of hydrated lime sorbents asprepared and degraded for 48 h and 168 h.

in the sense that is does not contain the capillarycondensation signature of the largest pores present [13]. The shapes of the pores also determine the type of the hysteresis loops. H3 hysteresis is usually found in solids consisting of aggregates or agglomerates of plate-like particles forming slit shaped pores with a nonuniform size and shape [14]. Overall, the isotherm hysteresis loops became small and the sorption capacity decreased with the process of degradation time. The asprepared sorbent and the sorbent degraded in the humid environment had aggregates of plate-like particles with slit shaped pores through the type of hysteresis loops.

Figure 4 indicates the pore size distribution plots obtained using the BJH method. The as-prepared sorbent and the sorbents degraded for 48h and 168h were measured. It can be seen that most of pores are mesoscale in the range of 20-1000 Å in diameter. It was assumed that the pores having a size range of 30~40 Å came from the presence of slit pores in interparticle or intraparticle regions and the pores over 100 Å were affected by large voids in the aggregates. The positions of the maximum in the pore diameter do not vary, but that of the pore volume significantly changed with elapsed degradation time. For the asprepared sorbent, the pore volume over the range from 30 Å to almost 40 Å was the highest value. After being exposed to the humid environment for 48 h, the total pore volume was decreased, in particular, the volume of pores having a diameter of about 35 Å was decreased abruptly. For the sorbent degraded for 168h, there is almost no porosity in this size range existing and pores in the range from 100 Å to 1000 Å were decreased slightly. In the degradation process, the pore volume of about 30-40 Å was reduced significantly, however, the volume of pores having sizes 100 Å - 1000 Å was little changed.

The change of the pore structure is likely the result of the clogging of small size pores due to the particle



Fig. 5. SEM morphologies and SAED patterns of (a,c) as-prepared and (b,d) degraded for 168 h sample.

aggregation and the carbonation process. Carbon dioxide (CO_2) diffuses from the environment into the pores of the calcium hydroxide sorbent, partly filled with water from the humidity. Then, the formation and the growth of calcium carbonate in the pores will contribute to a clogging of the pore structure [15] and the silt pores may also disappear due to the aggregation. Based on this pore collapse process, it is suggested that the exposure of hydrated lime sorbent to a humid environment decreases the pore volume and so its performance for SO₂ removal is reduced.

Figure 5 shows SEM morphologies of the asprepared sorbent and the sorbent degraded for 168 h. In our previous study [10], we have observed the morphologies of the sorbent produced by hydration of quicklime at a low magnification. At a higher magnification, the particles of the as-prepared sorbent (Fig. 5(a)) were aggregates of irregularly stacked small calcium hydroxide crystals with a 20-30 nm size. The sorbent degraded for 168 h in Fig. 5(b) shows a larger primary crystal size of 50-60 nm and significant aggregation of the crystals. The shape and size of the crystals became more regular and the aggregation had occurred severely compared to that of the as-prepared sorbent. The observed specific surface area reduction can be explained by taking into account the increased particle sizes and disappearance of voids or pores due to the aggregation as mentioned above.

In Fig. 5(c), the selected area electron diffraction (SAED) pattern of the as-prepared sorbent shows

continuous ring like patterns. The patterns indicate particles with a finer size and weak crystallinity. The SAED patterns of Fig. 5(d) show more evident and speckled patterns. It seems that the crystals have growth because of the aggregation process and calcite crystallization and so the ring patterns were made up of discrete spots.

Conclusions

The degradation behavior of hydrated lime sorbent exposed to a humid environment was studied in terms of pore clogging and pore collapse. The weight gains, which indicate a reactivity toward SO₂, were decreased from 120 wt% to 104 wt% with elapsed degradation time and the specific surface area was also decreased from 45.8 m²/g to 7.6 m²/g. The hydrated lime sorbents (portlandite) absorbed CO₂ gas from the environment which then resulted in turning into the calcium carbonate (calcite). This can be expected that CO_2 diffused into the pores of the hydrated lime sorbent, partly filled with water from the humidity, and then the formation and the growth of the calcium carbonate in the pores occur. Also the silt pores having a size range of 30~40 Å may also disappear owing to aggregation by humidity. Consequently, the decrease in the specific surface area concerning SO₂ removal efficiency was contributed to by pore clogging and pore collapse due to the carbonation process and the particle aggregation.

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