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Effect of $Ca(OH)_2$/fly ash weight ratio on the kinetics of the reaction of $Ca(OH)_2$/fly ash sorbents with SO_2 at low temperatures

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Abstract

$Ca(OH)_2$/fly ash sorbents were prepared with different weight ratios. Their reactions with SO_2 have been studied under the conditions similar to those in the bag filters of the spray-drying flue gas desulfurization system. The sorbent reactivity increased in general with decreasing $Ca(OH)_2$/fly ash weight ratio. The reaction kinetics was well described by the surface coverage model which assumes that the sorbent was made up of plate grains and the rate was controlled by the chemical reaction on the grain surface and takes into account the surface coverage by products. For sorbents with $Ca(OH)_2$/fly ash weight ratios than 10/90, the effect of weight ratio on the reaction was entirely represented by the effects of the intial specific surface area and the Ca content of the sorbent.

Keywords: Flue gas desulfurization; $Ca(OH)_2$; Kinetics; Mathematical modeling; Multiphase reaction; pollution

1. Introduction

Many researchers have shown that sorbents prepared from hydrated lime [$Ca(OH)_2$] and fly ash have higher SO_2 captures and Ca utilizations than hydrated lime alone has (Jozewicz and Rochelle, 1986; Ho, 1987; Ho and Shih, 1992, 1993; Garea et al., 1997a, b; Liu et al., 2002; Lin et al., 2003). Hence, the $Ca(OH)_2$/fly ash sorbents have a good potential for use in the dry and semidry flue gas desulfurization processes. The literature on the kinetic model for the reaction of $Ca(OH)_2$/fly ash sorbents with SO_2, however, is scarce. Garea et al. (1997b) proposed a nonideal surface adsorption model for sorbents with a $Ca(OH)_2$/fly ash weight ratio of $\frac{1}{3}$. Recently we reported a surface coverage model for sorbents with a weight ratio of 70/30 (Liu et al., 2002). In this work, the effect of $Ca(OH)_2$/fly ash weight ratio on the kinetics of the reaction of $Ca(OH)_2$/fly ash sorbents with SO_2 was investigated, with the aim to obtain a kinetic model for sorbents prepared with different $Ca(OH)_2$/fly ash weight ratios.

2. Experimental section

The $Ca(OH)_2$ reagent, fly ash, sorbent preparation procedure, and experimental setup and procedure for sulfation experiments used in this work were the same as those described in Liu et al. (2002) and Lin et al. (2003). Sorbents with different $Ca(OH)_2$/fly ash weight ratios, as those listed in Table 1, were prepared by first slurrying the solids at a water/solid weight ratio of 10/1 and 65 °C for 16 h and subsequently vacuum-drying the slurries at 105–110 °C for 8–10 h. The dry cake was crushed into powder. The mean particle diameters, d_p, of the sorbents were in the range of 4–35 µm, as shown in Table 1. The sorbents were made to react with SO_2 mainly at 60 °C, 70% relative humidity (RH) and 1000 ppm SO_2 using a differential fixed-bed reactor. For each run, about 30 mg of sample was dispersed into the quartz wool contained in the quartz sample pan, which had dimensions of 10 mm o.d. and 15 mm height.

The conversion, X, of a reacted sample was defined as its SO_3^{2-}/Ca^{2+} molar ratio. The SO_3^{2-}content in a sample was determined by iodometric titration, and the Ca^{2+} content by EDTA titration. The experimental error in X was about ±0.02.

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Table 1
$Ca(OH)_2$/fly ash weight ratios, sorbent weights per mole of Ca, mean diameters, BET specific surface areas, and values of k_1 and k_2^{-1} in Eq. (1) for $Ca(OH)_2$/fly ash sorbents

$Ca(OH)_2$/ Fly ash (wt. ratio)	M (g sorbent/mol Ca)	d_p (μm)	S_{g0} (m^2/g)	k_1 (min^{-1})	k_2^{-1}
Raw $Ca(OH)_2$	75	7	9.6	0.032	0.195
100/0	76	5	11.8	0.049	0.241
90/10	86	4	19.8	0.115	0.413
70/30	110	9	38.0	0.165	0.620
50/50	163	24	38.7	0.329	0.752
30/70	252	35	27.5	0.354	0.694
10/90	677	13	42.3	0.581	1.163

Slurrying conditions: 65 °C, $L/S = 10/1$, and 16 h. Reaction conditions: 60 °C, 70% RH, and 1000 ppm SO_2.

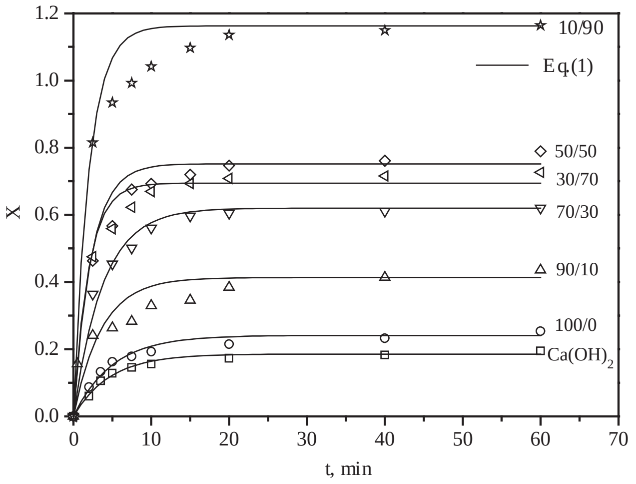

Fig. 1. Effect of $Ca(OH)_2$/fly ash weight ratio on the reaction of $Ca(OH)_2$/fly ash sorbents with SO_2. Slurrying conditions: 65 °C, $L/S = 10/1$, and 16 h. Reaction conditions: 60 °C, 70% RH, and 1000 ppm SO_2.

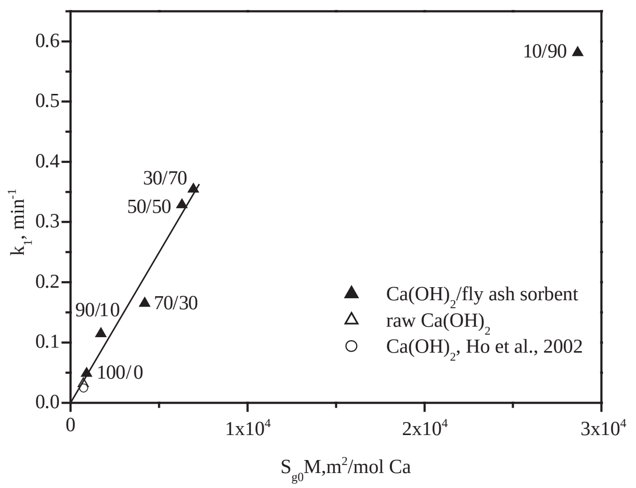

Fig. 2. Plot of k_1 versus $S_{g0}M$. Slurrying conditions: 65 °C, $L/S = 10/1$, 16 h. Reaction conditions: 60 °C, 70% RH, and 1000 ppm SO_2.

The Ca^{2+} content of a sorbent was determined by EDTA titration, and its reciprocal, M, the initial sorbent weight per mole of Ca, is listed in Table 1. The M value increases with decreasing $Ca(OH)_2$/fly ash weight ratio. The BET specific surface area, S_{g0}, of each sorbent is also listed in Table 1. The S_{g0} of a $Ca(OH)_2$/fly ash sorbent is much greater than that of $Ca(OH)_2$ alone due to the formation of foil-like calcium silicate hydrates in the sorbent (Liu et al., 2002; Lin et al., 2003).

3. Results and discussion

The experimental results for the reaction of the sorbents with SO_2 are shown in Fig. 1. In general, the sorbent reactivity increases with decreasing $Ca(OH)_2$/fly ash weight ratio. The reaction of each sorbent is seen to stop at an ultimate conversion after about a 20 min reaction time. The ultimate conversion of the sorbent with a ratio of 10/90 exceeds 1.0; this is because the contribution of the reactive compounds of Na, K, and Mg other than Ca present in the fly ash particles was also included when calculating the conversion.

The curves in Fig. 1 are the least-squares fitting curves of the data using the following equation given by the surface coverage model (Shih et al., 1999):

$$X = [1 - \exp(-k_1 k_2 t)]/k_2. \tag{1}$$

Like $Ca(OH)_2$ alone (Ho et al., 2002) and the sorbent with a ratio of 70/30 (Liu et al., 2002) the reaction behavior of the sorbents with other ratios are seen to be well described by the surface coverage model. The model assumes that the sorbent is made up of plate grains and the rate is controlled by the chemical reaction on the grain surface, and takes into account the surface coverage by products.

The values of k_1 and k_2^{-1} in Eq. (1) obtained for each sorbent are listed in Table 1. Both k_1 and k_2^{-1} values vary significantly with the $Ca(OH)_2$/fly ash ratio. However, as seen in Fig. 2, k_1 and $S_{g0}M$ for each sorbent follow a linear relationship, except the data for the sorbent with a 10/90 ratio. The linear least-squares fitting line in Fig. 2 gave

$$k_1(\text{min}^{-1}) = (5.00 \pm 0.22) \times 10^{-5} \times S_{g0}M, \tag{2}$$

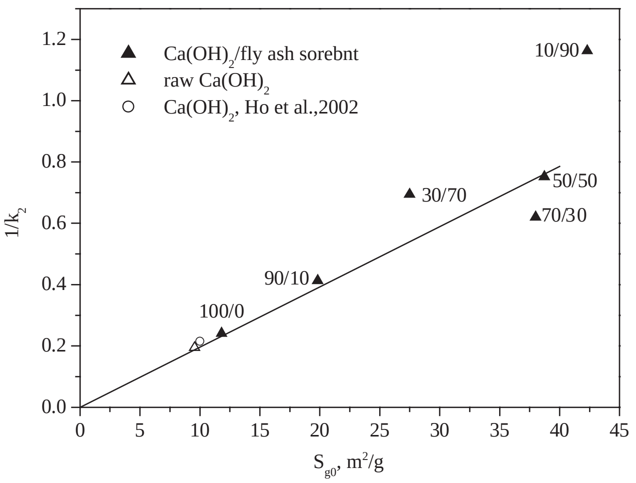

Fig. 3. Plot of k_2^{-1} versus S_{g0}. Slurrying conditions: 65 °C, $L/S = 10/1$, 16 h. Reaction conditions: 60 °C, 70% RH, and 1000 ppm SO_2.

with a correlation coefficient of 0.986. Furthermore, as shown in Fig. 3, there is a linear relationship between k_2^{-1} and S_{g0}, except the data for the sorbent with a 10/90 ratio. The linear least-squares fitting line in Fig. 3 gave

$$k_2^{-1} = (1.96 \pm 0.12) \times 10^{-2} \times S_{g0} \tag{3}$$

with a correlation coefficient of 0.945. According to Eq. (1), k_2^{-1} equals the ultimate conversion. Therefore, Eq. (3) implies that the ultimate conversion of a sorbent is proportional to its S_{g0} and independent of its M.

Eqs. (2) and (3) were obtained under the reaction conditions of 60 °C, 70% RH, and 1000 ppm SO_2. According to Ho et al. (2002) and Liu et al. (2002), k_1 and k_2 are also functions of RH, temperature, and SO_2 concentration, but only RH affects k_1 and k_2 significantly. In order to know whether the relationship between k_1 or k_2 and S_{g0} and M is affected by the RH, samples of $Ca(OH)_2$ ($M = 74$ g/mol Ca, $S_{g0} = 10.3\,m^2/g$) and the sorbent with a ratio of 30/70 ($M = 248$ g/mol Ca, $S_{g0} = 25.6\,m^2/g$) were reacted with 1000 ppm SO_2 at 60 °C and different RHs (30–80%). The $k_1/(S_{g0}M)$ and $k_2 S_{g0}$ values obtained were found to be well correlated with the RH using the correlations that have been given for the $Ca(OH)_2$/fly ash sorbent with a 70/30 ratio by Liu et al. (2002). Thus, the linear relationship between k_1 and $S_{g0}M$ or between k_2^{-1} and S_{g0} is valid at different RHs (30–80% RH). Furthermore, the equations representing the effects of RH, temperature (T), and SO_2 concentration (y) on k_1 and k_2 given in the article by Liu et al. (2002), Eqs. (13) and (14), are valid for sorbents with ratios $> 10/90$. Those two equations can be rewritten by combining with Eqs. (2) and(3), respectively, as

$$k_1 = 1.26 \times 10^{-4} S_{g0} M \mathrm{e}^{0.0234\mathrm{RH}} y^{0.10} \mathrm{e}^{-9096/RT}, \tag{4}$$

$$k_2 = 1930 S_{g0}^{-1} \mathrm{RH}^{-0.864}. \tag{5}$$

It should be noted that the numerical values of the parameters in Eq. (13) in the previous article were miswritten and should be corrected as

$$k_1 = 0.0112 S_{g0} \mathrm{e}^{0.0234RH} y^{0.10} \mathrm{e}^{-9096/RT}. \tag{6}$$

Conversions calculated by Eq. (1) together with Eqs. (4) and (5) were compared with the experimental results (Fig. 1) except those for the sorbent with a 10/90 ratio, both were in good agreement with a standard deviation of 0.07.

4. Conclusion

From the above analyses, we can conclude that for a $Ca(OH)_2$/fly ash sorbent prepared with a weight ratio larger than 10/90, its reaction with SO_2 at low temperatures can well be described by the surface coverage model, Eq. (1) together with Eqs. (4) and (5). The effect of $Ca(OH)_2$/fly ash weight ratio on the reaction kinetics was entirely represented by the effects of the initial specific surface area and the Ca content of a sorbent on the kinetic parameters.

Acknowledgements

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