KINETIC STUDY ON REACTIONS OF H₂S WITH LIMESTONE AND HALF-CALCINED DOLOMITE

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Reactivities of two sorbents, a limestone and a half calcined dolomite, with H₂S under simulated pressurized coal gasification conditions were studied by using TGA techniques. Although the activation energies for both sorbents are found to be about 180 kJ·mol⁻¹, the initial reaction rate of the half-calcined dolomite (50 μm) is about 30 times faster than that of the limestone (50 μm). The reactions of both materials are first order with respect to H₂S partial pressure. The pressure of CO₂ and H₂O has almost no effect on the sulfidation reaction of the half calcined dolomite, but has adverse effects on the reaction of the limestone. Although, in general, the smaller particles can react faster, it is found that the effect of particle size on the reaction rate is different, with $d_p^{-0.17}$ for the half calcined dolomite and $d_p^{-0.85}$ for the limestone.

Introduction

Coal-combined power generation, such as IGCC and Topping cycle (second PFBC), are expected to realize much higher efficiency if sulfur compounds in the flue gas can be removed under high temperature and pressure. High-temperature H₂S capture may be performed by injecting calcium-based sorbents such as limestone (CaCO₃) and dolomite (CaMg(CO₃)₂) into the coal gasifier. If the gasifier is operated under atmospheric conditions, limestone and dolomite will decompose, having calcined limestone (CaO) and dolomite (CaMgO₂) to react with H₂S. If the gasifier is operating under high pressure, the partial pressure of CO₂ in the gasifier may become higher and will hinder the decomposition of carbonates. Raising the operating temperature is favorable for the decomposition of CaCO₃, but the higher temperature will enhance sintering of CaO and CaS and formation of slag in the ash.

When the partial pressure of CO₂ is eventually higher than that of the equilibrium CO₂ partial pressure for CaCO₃ decomposition, only MgCO₃ will decompose and there will be no decomposition of CaCO₃. It can be considered that the following sulfidation reactions would occur when using limestone or dolomite for H₂S removal in the pressurized gasifier.

for limestone:

for dolomite:

In both equations 1) and 3), sulfidation is the reaction of CaCO₃ with H₂S. Although several studies have been made on the sulfidation of CaCO₃ with H₂S, the results reported differ in many cases. For example, Borgwardt and Roache (1984) reported that the reactivity of limestone was reduced by increasing CO₂ and H₂O partial pressures, but Ruth *et al.* (1972) reported that the reactivity of a half calcined dolomite was increased with increasing CO₂ and H₂O partial pressures. No reason and investigation were available in detail. This may be confusing when evaluating the CaCO₃-H₂S reaction and to predict the conditions of the gasifier by using Ca-Mg based sorbents. The change in solid structure and the presence of other substances like MgO in half calcined dolomite may have some role during the reaction of CaCO₃ with H₂S. However, both information and reaction kinetics concerning the sulfidation of half calcined dolomite and limestone are rather scant.

Accordingly, to classify the characteristics of H₂S reaction with half calcined dolomite and limestone at high CO₂ partial pressure, in this work, attention was focused on the effects of the composition of CO₂ and H₂O gases, as well as particle size. From the results obtained, an empirical reaction rate equation has been developed.

1. General Features of the Half-Calcination of Dolomite

Dolomite is composed of CaCO₃ and MgCO₃. Based on thermodynamic data derived from Barin

Fig. 1 Equilibrium CO_2 partial pressure for calcination of CaCO_3 and MgCO_3

Fig. 2 Equilibrium $P_{\text{H}_2\text{S}}$ partial pressure and equilibrium temperature for sulfidation of CaCO_3 and MgO

Table 1 Chemical composition of limestone and dolomite [wt%]

	CaCO_3	MgCO_3	Al_2O_3	MnO	H_2O
Chichibu limestone	98.1	1.67	0.24	0.04	0.04
Tochigi dolomite	61.4	38.0	—	—	—

(1989), the relationships between temperature and CO_2 equilibrium partial pressure for the decomposition of CaCO_3 and MgCO_3 are shown in Fig. 1. From this figure, it can be seen that above 600 K, the equilibrium CO_2 pressure for MgCO_3 is larger than 100 kPa, which is much higher than the CO_2 pressure possible in the pressurized gasifier. Since the equilibrium pressure of CO_2 during the decomposition of CaCO_3 is only 48 kPa at 1123 K, it is considered that, if MgCO_3 and CaCO_3 are heated under a certain CO_2 partial pressure, the decomposition of MgCO_3 in the dolomite will firstly occur at lower temperatures, followed by the decomposition of CaCO_3 at much higher temperatures. Thus, when dolomite is heated under a certain pressurized gasifier condition (for example at 100 kPa CO_2 and 1073 K), it is possible to attain a half calcined dolomite without decomposing the CaCO_3 component in the dolomite.

By using the thermodynamic data of Barin (1989), the equilibrium $P_{\text{H}_2\text{S}}$ -temperature relationships for sulfidation of MgO and CaCO_3 with partial pressures of H_2O and CO_2 fixed at 78 kPa and 101 kPa, respectively, for a simulating pressurized gasifier condition (total pressure is 10 atm), can be constructed as in Fig. 2. If the gas atmosphere existing in a coal gasifier is in the range of 78 kPa $P_{\text{H}_2\text{O}}$, 101 kPa of P_{CO_2} , and 5 kPa of $P_{\text{H}_2\text{S}}$, it can be considered that no sulfidation reaction of MgO would take place in the gasifier.

The other fundamental phenomena for the problem of relating sulfidation kinetics to the properties of

a half calcined dolomite may be the structural and morphological changes which take place during half-calcination. Haul and Wilsdorf (1951) and Siegel *et al.* (1978) investigated the half-calcined dolomite crystals by X-ray diffraction and microscopy. They indicated that the dolomite crystals had undergone reduction in size during the half-calcination and were replaced with an apparent single crystal of calcite. The crystallite size and disorder are regarded as having an important bearing on the calcite reactivity.

2. Experimental Section

2.1 Samples

Tochigi dolomite and Chichibu limestone (Japan) of 5–1000 μm diameter were used as the starting materials. Table 1 shows the chemical composition of these materials.

2.2 Thermogravimetric experiments

Figure 3 shows a schematic diagram of the thermobalance (SHIMADZU-TG-20) used to measure the sulfidation rates. The reaction tube (18 mm i.d. and 100 mm length) was made of alumina. A continuous flow of $\text{H}_2\text{S}/\text{H}_2/\text{CO}_2/\text{N}_2$ and water vapor was fed into the upper part of the reaction tube, and it flowed downward onto the sample. The sample pan (2 mm high and 4 mm i.d.) was made of platinum. The total gas flow rate was set at $1.67 \times 10^{-6} \text{ m}^3 \cdot \text{s}^{-1}$. Since the changes in reaction rate were very slight when the gas flow was increased to $2.5 \times 10^{-6} \text{ m}^3 \cdot \text{s}^{-1}$, it was considered that the gas flow rate of $1.67 \times 10^{-6} \text{ m}^3 \cdot \text{s}^{-1}$ was

Fig. 3 Schematic diagram of TGA experimental apparatus

sufficient to overcome the gas film resistance.

In the presence of CO_2 gas, H_2S may react with CO_2 according to the reaction:

Thermodynamic equilibrium calculations given by Krishnan and Sotirchors (1994) indicated that in a gas mixture containing 70 vol% CO_2 , 0.05 vol%, and H_2S 29.4 vol% N_2 at 1023 K, nearly 85% of the H_2S will react according to Eq. (4). However, they also reported that less than 3% of the H_2S was really converted in their TGA experiment under the same conditions. The reason may be that the time required for reaching the equilibrium concentration would be very long. On the other hand, Fenouil *et al.* (1994) found that the pressure of 4 vol% H_2 in a gas mixture of 95 vol% CO_2 and 1 vol% H_2S would hinder the progress of the reaction between CO_2 and H_2S . Therefore, in order to prevent the reaction between CO_2 and H_2S , 6 vol% of H_2 was added to the feed gas stream in our experiments.

2.3 Procedure

About 1×10^{-6} kg of sample was spread evenly in the sample pan and heated at a constant heating rate of $0.83 \text{ K} \cdot \text{s}^{-1}$. Each sample was heated under CO_2 atmosphere to avoid CaCO_3 decomposition. For sulfidation of dolomite, the sample was first half calcined under a CO_2 atmosphere at 1123 K for about 10 minutes, and then the temperature was changed to the desired sulfidation temperature. Sulfidation was initiated by changing the gas stream to a predetermined $\text{CO}_2/\text{H}_2/\text{H}_2\text{S}/\text{N}_2$ and water vapor gas mixture. The sulfidation temperature range was 1023 – 1143 K.

2.4 Sample characteristics

The specific surface areas of the sample before and after sulfidation were measured by an N_2 adsorption technique (SHIMADZU ASAP 2000). These measurements covered the pores ranging from 10 to $10^3 \text{ \AA}$. The morphology of the particle surface

Table 2 Specific surface area of dolomite sample for various calcination times (1123 K, CO_2 100 kPa) $\times 10^{-3} [\text{m}^2 \cdot \text{kg}^{-1}]$

Natural dolomite	Half calcination time		
	10 min	55 min	70 min
0.13	5.75	4.98	4.36

Table 3 Comparison of specific surface area of dolomite half calcinated with and without presence of water vapor (1123 K, CO_2 balance) $\times 10^{-3} [\text{m}^2 \cdot \text{kg}^{-1}]$

Without steam	With steam		
	5.75 vol%	10.98 vol%	23.48 vol%
5.75	4.83	4.70	4.59

of the sample taken after sulfidation was examined by a scanning electron microscope (SEM).

3. Results and Discussion

3.1 Reactants and products analysis

Table 2 shows the specific surface area of dolomite calcined under various conditions. It can be seen that the half calcination of dolomite created new surfaces and increases the specific surface area to $5.7 \times 10^3 \text{ m}^2 \cdot \text{kg}^{-1}$, more than 40 times the surface area available in natural dolomite, which is only $0.13 \times 10^3 \text{ m}^2 \cdot \text{kg}^{-1}$. Extending the heat treatment time has only a slight effect on the surface area, e.g., even when the heat treatment was as long as 60 minutes, the surface area of the calcined sample was only reduced to $4.4 \times 10^3 \text{ m}^2 \cdot \text{g}^{-1}$. The presence of steam during heat treatment also did not have a significant effect on the specific surface area (see Table 3).

Figure 4 shows the pore size distribution of dolomite at various stages of calcination. From this figure, it can be seen that pore volume of the sample increases after calcination. However, the range of pore sizes shifted only a little towards the larger size range when the sample was continuously heated for 60 minutes.

As the specific surface area of 1 mm Chichibu limestone measured by ASAP is about $0.19 \text{ m}^2 \cdot \text{g}^{-1}$ (Lin *et al.*, 1995), it can be concluded that the porosity of the limestone is very low.

Borgwardt (1989, a, b) and Anderson and Morgan (1964) reported that the specific surface area of the CaO and MgO are reduced during heat treatment and the surface area reducing rate was enhanced with the presence of CO_2 and H_2O . However, Fenouil *et al.* (1994) reported that no significant change in pore structure of limestone (CaCO_3) was found when limestone was heated in the temperature

Fig. 4 Pore size distributions of dolomite, half-calcined dolomite and after half-calcination of about 10 minutes

range 1023 – 1173 K under 101 kPa CO₂. No significant change in the specific surface area of the half calcined dolomite during heat treatment may be due to the scattered presence of CaCO₃ crystallites obstructing the sintering of MgO.

3.2 Reactivity of half calcined dolomite and limestone

The fractional conversions of CaCO₃ to CaS, X , based on weight loss for the sulfidation of both half calcined dolomite and limestone were calculated by the relationship:

$$X = \frac{M_{\text{CaCO}_3} \cdot W_{\text{L},s}}{w_0 \cdot F_{\text{CaCO}_3} \cdot (M_{\text{CaCO}_3} - M_{\text{CaS}})} \quad (5)$$

Figure 5 shows the conversion of CaCO₃ to CaS vs. time for both half-calcined dolomite and limestone. The sulfidation rate and final conversion of half-calcined dolomite were much higher than those of limestone. Although dolomite is composed of MgO, which has low reactivity toward H₂S under low $P_{\text{H}_2\text{S}}$, conversion of almost 100% of CaCO₃ in half-calcined dolomite to CaS, in contrast to conversion of 17% CaCO₃ in limestone indicates that H₂S captivity of the half calcined dolomite is much higher than the limestone. This difference in reactivity between the half calcined dolomite and the limestone may be attributed to the fact that the half-calcined dolomite has higher specific surface area.

For a sulfidation reaction of the type $\text{M} \cdot \text{CO}_3 + \text{H}_2\text{S} \rightarrow \text{M} \cdot \text{S} + \text{CO}_2 + \text{H}_2\text{O}$, the reaction rate can be expressed as:

$$\left(\frac{dX}{dt} \right)_{X \rightarrow 0} = d_p^m \cdot k \cdot P_{\text{H}_2\text{S}}^{n_1} \cdot P_{\text{CO}_2}^{n_2} \cdot P_{\text{H}_2\text{O}}^{n_3} \quad (6)$$

where

Fig. 5 Sulfidation of limestone and half calcined dolomite

Fig. 6 Sulfidation rate dX/dt for half-calcined dolomite and limestone under various conditions

$$k = k_0 \cdot \exp\left(\frac{-E}{R \cdot T}\right) \quad (7)$$

The first term on the right hand side of Eq. (6) is the effect of particle size which relates to the reaction pattern occurring in the particle.

3.3 Temperature effects on sulfidation rate

Figure 6 shows the typical Arrhenius plot of initial reaction rate dX/dt for both limestone and half-calcined dolomite. Several results from previous studies are also shown in this figure.

For limestone, although the results slightly differ due to different materials and different particle sizes, the apparent activation energy is the same at about 180 kJ·mol⁻¹. It can be seen that the reaction rate still follows a linear pattern even when the sulfidation experiments were carried out at temperatures as high as 1143 K. The linearity indicates that it is controlled by chemical reaction and it is probably occurring only on the outside surface of the particle.

Since the apparent activation energies for

Fig. 7 Effect of H_2S partial pressure on sulfidation of half-calcined dolomite and limestone

limestone and half calcined dolomite are almost the same, the reaction during sulfidation of half calcined dolomite will be similar to that of limestone, as $CaCO_3 + H_2S = CaS + CO_2 + H_2O$.

Though the reaction rate of half calcined dolomite is about 20–30 times faster than the rate of limestone (which may be due to large differences in surface areas), it deviates from linearity at about 1073 K with a slight drop in reactivity, indicating that at higher temperatures, diffusivity and other factors will control the reaction, even at its initial reaction stage.

3.4 H_2S effect

The effect of H_2S partial pressure on the initial reaction rate for sulfidations of limestone and half calcined dolomite are shown in Fig. 7. Since the initial sulfidation rates for both sorbents linearly increases with the increase in P_{H_2S} , it is concluded that the reactions are first order with respect to P_{H_2S} . Thus the exponent n_1 for P_{H_2S} in equation (6) is equal to 1.

3.5 CO_2 and H_2O effects

It has been indicated that the presence of H_2O and CO_2 do not significantly influence the solid structure of limestone and half calcined dolomite. In the following, we will further discuss the effect of CO_2 and H_2O on the reaction rate.

When limestone is sulfidated under various CO_2 partial pressures (30–60 kPa), it is found that the initial sulfidation rate decreases linearly with the increase in P_{CO_2} (Fig. 8). Thus, the exponent n_2 for P_{CO_2} in the sulfidation rate expression Eq. (6) is equal to (–1).

Also, when limestone is sulfidated under various H_2O partial pressures (0.3–3 kPa), although the reaction rate decreases linearly with the increase in H_2O partial pressure, the slope of the relationship is about –0.55. Thus, for limestone, the $P_{H_2O}^m$ term in reaction rate expression Eq. (6) will become $P_{H_2O}^{-0.5}$ (refer Fig. 9).

However, when the half-calcined dolomite is sulfidated under 10–60 kPa CO_2 and under 0–7 kPa

Fig. 8 Effect of CO_2 partial pressure on sulfidation of limestone

Fig. 9 Effect of water vapor on sulfidation rate of limestone

H_2O partial pressures, the reaction rate is found to be constant, indicating that the reaction rate is zero order with respect to P_{CO_2} and P_{H_2O} (refer Figs. 10 and 11). This in turn means that the reverse reaction is of no significance on half-calcined dolomite sulfidation. It can also be verified from Figs. 12 and 13 that within the experimental range of P_{CO_2} (20–50 kPa) and P_{H_2O} (0–6.6 kPa), half-calcined dolomite attains complete conversion within 10–15 minutes for all sulfidation experiments.

3.6 Particle size effect

In Eq. (6), exponent m for particle size d_p may take a value between –1–0. When reaction occurs uniformly and evenly over the whole particle, $m=0$, and when the reaction occurs only on the outside surface of the particle, $m=-1$.

Figures 14 and 15 show the effect of particle size on sulfidation of limestone and half calcined dolomite. It can be seen that the initial reaction rate of the small particle is higher than that of the larger particle. The exponent m was found to be –0.85 for limestone and –0.17 for half calcined dolomite. Since –0.85 is close to –1, it can be considered that the sulfidation of limestone will occur mostly on the outer crust of the particle, whereas the exponent of –0.17 indicates that the sulfidation reaction of half-calcined dolomite will

Fig. 10 Effect of CO₂ partial pressure on sulfidation rate of half-calcined dolomite

Fig. 11 Effect of water vapor on sulfidation rate of half-calcined dolomite

Fig. 12 Effect of CO₂ partial pressure on sulfidation of half-calcined dolomite and limestone

occur uniformly throughout the particle, even in the initial reaction step.

3.7 Reaction rate expression

Accordingly, by using Fig. 6 and the results

Fig. 13 Effect of water vapor on sulfidation of half-calcined dolomite and limestone

Fig. 14 Effect of particle size on sulfidation of limestone

Fig. 15 Effect of particle size on sulfidation rate of half-calcined dolomite

obtained in the previous sections, the reaction rate constant k and its coefficient k_0 can be evaluated by means of Eqs. 6 and 7. From the calculation, k_0 for half-calcined dolomite and limestone are found to be 4.75×10^2 and 1.68×10^4 [$\text{m} \cdot \text{Pa}^{-1} \cdot \text{s}^{-1}$], respectively. Thus, the reaction rate equation (Eq. (6)) will become:

for half calcined dolomite (~1073 K):

$$\left(\frac{dX}{dt}\right)_{X \rightarrow 0} = d_p^{-0.17} \cdot 4.75 \times 10^2 \cdot \exp\left(\frac{-21650}{T}\right) \cdot P_{\text{H}_2\text{S}}$$

for limestone (~1143 K):

$$\left(\frac{dX}{dt}\right)_{X \rightarrow 0} = d_p^{-0.85} \cdot 1.68 \times 10^4 \cdot \exp\left(\frac{-21650}{T}\right) \cdot P_{\text{H}_2\text{S}} \cdot P_{\text{CO}_2}^{-1} \cdot P_{\text{H}_2\text{O}}^{-0.5}$$

When the gasifier operates at a high temperature, which is higher than the equilibrium temperature for CaCO_3 decomposition, the limestone (CaCO_3) will be calcined to form CaO , and the dolomite ($\text{CaMg}(\text{CO}_3)_2$) will be calcined fully to form CaMgO_2 . **Figure 16** shows the sulfidation data for dolomite and limestone under conditions (1173 K, CO_2 60 kPa) where dolomite and limestone can be calcined fully. It can be seen that the reaction rate of the fully calcined dolomite can also be higher than those of the calcined limestone.

Conclusion

The reactivity of H_2S with a half-calcined dolomite and a limestone are studied in order to enhance sulfur capture in pressurized coal gasification processes, since efficient sulfur removal under high temperature and pressure is one of the major issues encountered in gasifier operation.

It is found that although about half of the dolomite is composed of MgO which is not so much reactive toward H_2S under gasifier conditions, half-calcined dolomite can convert nearly all of its CaCO_3 component into CaS , in contrast to that of limestone, which is composed of almost 100% CaCO_3 , can convert about 20% of its sorbent into CaS . Moreover, the initial reaction rate of half calcined dolomite (50 μm) is about 30 times higher than that of limestone (50 μm). However, the activation energies are found to be the same, at about $180 \text{ kJ} \cdot \text{mol}^{-1}$ for both sorbents, indicating that the actual sulfidation taking place in both sorbents would only be that of $\text{CaCO}_3 + \text{H}_2\text{S} = \text{CaS} + \text{H}_2\text{O} + \text{CO}_2$. Also the reaction rate for both sorbents is found to be first order with respect to the partial pressure of H_2S . Although the rate of half calcined dolomite is not affected by variation in the partial pressures of CO_2 and H_2O , the rate of limestone decreases with an increase in the partial pressure of CO_2 and/or H_2O .

Sulfidation with various particle sizes indicates that the sulfur capture reaction can occur uniformly throughout the half calcined dolomite particle, whereas it can occur only on the thin layer of the

Fig. 16 Sulfidation of full calcined dolomite and calcined limestone at 1173 K

surface of the limestone particle.

From the results obtained, the sulfidation reaction rate can be expressed as:
for half calcined dolomite:

$$\left(\frac{dX}{dt}\right)_{X \rightarrow 0} = d_p^{-0.17} \cdot 4.75 \times 10^2 \cdot \exp\left(\frac{-21650}{T}\right) \cdot P_{\text{H}_2\text{S}}$$

for limestone:

$$\left(\frac{dX}{dt}\right)_{X \rightarrow 0} = d_p^{-0.85} \cdot 1.68 \times 10^4 \cdot \exp\left(\frac{-21650}{T}\right) \cdot P_{\text{H}_2\text{S}} \cdot P_{\text{CO}_2}^{-1} \cdot P_{\text{H}_2\text{O}}^{-0.5}$$

Nomenclature

d_p	= particle diameter	[m]
$i.d.$	= inside diameter	[m]
F_{CaCO_3}	= fraction of CaCO_3 sample	[—]
k	= reaction constant	$[\text{m} \cdot \text{Pa}^{-1} \cdot \text{s}^{-1}]$
k_0	= coefficient of k	$[\text{m} \cdot \text{Pa}^{-1} \cdot \text{s}^{-1}]$
m	= exponent in Eq. (6)	[—]
M_{CaCO_3}	= molecular weight of CaCO_3	$[\text{kg} \cdot \text{kmol}^{-1}]$
M_{CaS}	= molecular weight of CaS	$[\text{kg} \cdot \text{kmol}^{-1}]$
n_1, n_2, n_3	= exponents in Eqs. (6)	[—]
$P_{\text{H}_2\text{O}}$	= partial pressure of water vapor	[Pa]
$P_{\text{H}_2\text{S}}$	= partial pressure of H_2S	[Pa]
$P_{\text{CO}_2}^*$	= equilibrium partial pressure of CO_2	[Pa]
P_{CO_2}	= partial pressure of CO_2	[Pa]
PFBC	= pressurized fluidized-bed combustor	
$W_{\text{L,S}}$	= weight loss upon sulfidation of sample	[kg]
w_0	= weight of sample at time 0	[kg]
X	= fractional conversion of CaCO_3 into CaS	[—]

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