Effect of particle size on thermal decomposition of lime shells: Suitability of calcined lime shell for pollution control and energy storage

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Lime shells obtained from the lagoons of Kerala Coast have been decomposed with a view to study the effect of particle size. A modified TGA has been used to study the decomposition kinetics at various temperatures. Conversion time data obtained showed typical sigmoidal behaviour and the decomposition kinetics could be fitted to the Prout-Tompkins model at all temperatures and for all particle sizes studied. Arrhenius kinetic parameters showed normal type of compensation behaviour indicating an isokinetic temperature of 730°C. A theoretical explanation for these observed compensation behaviour and isokinetic temperature has been given. Further, the calcined lime shell has been tested for the capture of CO₂ and SO₂ using TGA. Effects of temperature of decomposition and particle size have been studied in this case. A theoretical, explanation based on pore size distribution of the calcined lime for this special behaviour has been given.

A very pure form of CaCO₃ is available abundantly in the backwaters of Kerala and Karnataka coasts in the form of lime shell or sea shell. It is being extensively used in calcium carbide and cement industries and also in the treatment of acidic spent liquors. Due to its high purity and low cost it is a good candidate for use in chemical industries as well. Lime shell has to be calcined at high temperature to convert CaCO₃ into CaO before it is used in chemical industries. Literature on the calcination of the lime shells is very much limited. Hence in the present study, calcination of these lime shells has been studied in detail with a view to understand effect of particle size. Studies also have been made on the use of calcined product (CaO) for the capture of CO₂ and SO₂ gases so that the suitability for energy storage and pollution control of these calcined products could be established.

Experimental Procedure

Materials

Lime shell containing about 99% CaCO₃ and less than 0.1% Fe₂O₃ were supplied by Travancore Electrochemical Industries, Chingavanam, Kerala State. The shells were dried and crushed before being classified into various size fractions. CO₂ and SO₂ of high purity (stored in cylinders) were supplied by local firms of repute.

Apparatus

For kinetic studies, a manually operated thermogravimetric analyzer (TGA) was employed. It consisted of a Kanthal wound quartz reactor mounted vertically in a tubular furnace, modified Mettler microbalance and a shock- and vibration-proof stand over which the reactor assembly with balance was mounted.

Method

A silica pan (dia.=2.5 mm, ht=17 mm) containing 1.0g of lime shell sample was introduced into the reactor with a constant air flow (22.0 mL/s) at desired temperature. The conversion time data of decomposition were collected at four temperatures (660°C, 690°C, 720°C and 750°C) by continuous monitoring of weight change. The lime shell used in the decomposition study consisted of three particle sizes. To study the CO₂ capture, the lime shell (0.500 g) was decomposed at 700°C (18.5 mol/s) containing 24% CO₂. The conversion-time data were collected at 600°C by continuous monitoring of the weight change. Similarly, the capture of SO₂ was studied at 700°C in a steady flow of SO₂ (4 mL/s) and air (31 mL/s). The conversion-time data were collected by continuous monitoring of the weight gain. About
0.500 g of the calcined sample was maintained at the desired temperature for 20 min before passing of reactive gas.

Results and Discussion

Decomposition of lime shells

Conversion-time data of lime shell decomposition at various temperatures showed typically sigmoidal behaviour. It consisted of an initial slow decomposition rate accompanied by fast reaction rate and finally a deceleration in rate towards the end of decomposition. Initial slow decomposition rate is characterized by the formation of nuclei of reaction product and this period is also called “Induction Period”. The induction period is followed by an accelerating rate of decomposition when the product formed is known to catalyze the decomposition rate and hence this step is referred to as an autocatalytic process, which covers a wide range of conversion for the decomposition reaction. The final deceleration step is the result of exhaustion of reacting solid during the first two steps and here, reaction rate drops slowly to zero. The whole picture of this decomposition can be modeled using a solid state reaction model proposed by Prout and Tompkins:

\[ \log \frac{x}{1-x} = kt + C \]  ... (1)

where, \( x \), \( k \) and \( t \) refer to fractional conversion, rate constant and the reaction time respectively, \( C \) is a constant. The experimental data of decomposition of lime shell of various particle sizes, were fitted to this kinetic model by plotting \( \log \frac{x}{1-x} \) versus time \( t \). The model plots of the decomposition runs at various temperatures were smooth straight lines confirming that the reaction followed the autocatalytic path. From the slope of the model plots the values of the rate constant \( k \) were calculated and shown in Table 1. Figs 1 and 2 are the typical decomposition data and model plots respectively. From the Table 1 it is seen that the decomposition rate increases with increase in temperature for a given particle size of the lime shell and it also increases with decrease in a particle size for a given temperature up to the decomposition temperature 700°C and near about 750°C the rate constant \( k \) seems to be independent of particle size. This fact was further investigated by constructing Arrhenius plot and evaluating one activation energy \( (E) \) and frequency factor \( (A) \) for the various size ranges of the particle studied. It is seen that activation

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>Rate Constant ( k ) sec(^{-1} ) for particle size (( \mu m ))</th>
</tr>
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<tbody>
<tr>
<td>660</td>
<td>1.58x10(^3 ) 2.54x10(^3 ) 2.77x10(^3 )</td>
</tr>
<tr>
<td>690</td>
<td>2.84x10(^3 ) 3.22x10(^3 ) 3.74x10(^3 )</td>
</tr>
<tr>
<td>720</td>
<td>4.67x10(^3 ) 5.04x10(^3 ) 5.14x10(^3 )</td>
</tr>
<tr>
<td>750</td>
<td>6.57x10(^3 ) 6.74x10(^3 ) 6.57x10(^3 )</td>
</tr>
</tbody>
</table>

Arrhenius Parameters

<table>
<thead>
<tr>
<th>( E ), Kcal/mole</th>
<th>( A )</th>
</tr>
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<tbody>
<tr>
<td>32.16</td>
<td>5.89x10(^3 )</td>
</tr>
<tr>
<td>20.98</td>
<td>20.98</td>
</tr>
<tr>
<td>17.81</td>
<td>17.81</td>
</tr>
<tr>
<td>88</td>
<td>42.70</td>
</tr>
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Fig. 1—X-t plots for calcination of lime shell

Fig. 2—Model plots for calcination of lime shell
energy and frequency factor show a typical compensation relationship expressed by

\[ \log A = mE + C \quad \ldots \quad (2) \]

where \( mE \) and \( C \) are constant. Alternatively Eq. 2 can be written as

\[ \log A = -\frac{E}{2.303RB} + \log k \quad \ldots \quad (3) \]

where \( B \) is isokinetic temperature. A typical compensation effect plot constructed by plotting \( \log k \) versus \( 1/T \) for various particle sizes indicated that all the plots were interesting at a single point called isokinetic temperature (Fig. 3). In the present case isokinetic temperature (B) of 730°C was noticed and it corresponds to the condition at which rate constant is independent of particle size. This is a novel behaviour observed for the first time in the decomposition of CaCO₃ species. In the decomposition studies of various particle sizes two opposing forces (which are strong functions of temperature) are in operation. The decomposition rate increases with decrease in particle size due to the increase in specific surface area. However, heat transfer rate becomes higher in the case of larger particle due to its compactness (for the same weight of lime shell). Hence the observed isokinetic temperature of 730°C is due to the two simultaneous but opposing effects influencing the rate of the observed behaviour (\( \Delta H=43.2 \text{ Kcal / mole} \)).

Capture of CO₂ and SO₂ by calcined lime shell

During the capture of CO₂ by lime considerable amount of heat is evolved and the decomposition of calcium carbonate is an endothermic reaction. Hence capture of CO₂ by CaO is used in energy storage¹. Moreover, the reaction of SO₂ with lime is universally popular process for pollution control. In the present study lime shells calcined at 700°C and 900°C used for capture of these gases with a view to study the effect of calcination temperature on the reactions related to energy storage and pollution control. Two size fractions of lime shell (420 and 102 \( \mu \text{m} \)) were decomposed at 700°C and 900°C separately and typical CO₂ capture data at 600°C and SO₂ capture data at 700°C have been shown in Fig. 4. The kinetic data were fitted to the Ginstling-Brounstein equation:

\[ 1+(Z-1)X]^{2Z}+(Z-1)(1-x)^{2Z}-Z=2(1-Z)kt/r^2 \quad \ldots \quad (4) \]

where,

\[ Z = \frac{\text{Volume of product formed}}{\text{Volume of reactant consumed}} \quad \ldots \quad (5) \]

In the present case \( Z=3.1345 \) for CaO + \( \frac{1}{2} \text{O}_2 \) reaction and \( Z=2.2194 \) for CaO=CO₂ Eq. (4). Typical kinetic plots using the above model were found to be straight lines. From the slope of plots the rate constants \( k \) were evaluated at various conditions studied.

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Conclusion

For both the particle sizes SO₂ capture rate was higher in the case of lime shell calcined at 700°C. This may be attributed to the differences in mean pore radius of the calcined lime shell. The lime shell (420 μm) calcined at 700°C and 900°C had mean pore radii of 0.126×10⁻⁴ cm and 0.117×10⁻⁴ cm respectively. Also it is well known that during CO₂ capture, sintering of CaO matrix is catalyzed by CO₂. But during SO₂ capture no such catalyzed sintering is reported. Hence during CO₂ capture, rate constants vary to the extent of 30-37% (for the same sized samples calcined at 700°C and 900°C) and during SO₂ capture, the rate constants vary to the extent of 17 to 20% only. The calcined lime shell has been found to be quite useful in energy storage and SO₂ pollution abatement.

References