A Kinetic Model of Nano-CaO Reactions with CO₂ in a Sorption Complex Catalyst

S. F. Wu and P. Q. Lan
Dept. of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310027, China

DOI 10.1002/aic.12675
Published online June 10, 2011 in Wiley Online Library (wileyonlinelibrary.com).

This article describes the reactive kinetics of nano-CaO with CO₂ in a sorption complex catalyst. Based on an observation of nano-CaO reaction with CO₂ has a fast surface reaction regime and followed by a slow diffusion-controlled regime, a criterion has been proposed to divide the fast surface reaction regime and the slow diffusion-controlled reaction regime. The kinetics of the fast surface reaction was studied, and a new ion reaction mechanism was proposed. A surface reaction-controlled kinetic model with a Boltzmann equation,

\[ X = X_u - X_u(1 + \exp(-(t-t_0)k/X_u))] \]

Experiments using nano-CaO to react with CO₂ in a fast surface reaction regime within a sorption complex catalyst were performed using thermogravimetric analysis at 773–873 K under a N₂ atmosphere with 0.010–0.020 MPa CO₂. The activation energy of the kinetic model for carbonation is 30.2 kJ/mol, and the average relative deviation of the sorption ratio is less than 9.8%. © 2011 American Institute of Chemical Engineers

Keywords: CO₂ capture, carbonation, kinetics, nano-CaO, sorption complex catalyst

Introduction

Hydrogen is an important raw material in the chemical and petroleum industries and plays a major role in developing economies. Hydrogen is of particular interest because it is also used for the generation of electric power and employs highly efficient fuel cells. Approximately 95% of the H₂ currently produced in the US uses the steam-methane reforming process. The sorption-enhanced reaction process has the advantages of high thermal efficiency, low economic investment and CO₂ capture. A reaction sorption-enhanced reaction (ReSER) process is one type of sorption-enhanced reaction process. The key points of the ReSER system are the use of nano-CaO as the reactant with CO₂, a sorption complex catalyst and a circulating fluidized bed system. Nano-CaO has been identified as the most promising reactant because it has a rapid reactivity with CO₂, high reactive sorption capacity, high durability, low decomposition temperature and abundant natural precursors. Most importantly, the fast reaction of nano-CaO with CO₂ plays an important role in the ReSER process for hydrogen products.

The chemical reaction of CaO with CO₂, as shown in Eq. 1, is highly exothermic. The reaction rate of CaO with CO₂ affects the reaction rate of the steam methane reforming reaction. The reason for the enhanced reforming reaction is that removing the product will break the thermodynamic equilibrium of a reversible reforming reaction according to the Le Chatelier principle. The same result of enhanced reforming is achieved by removing the hydrogen product using hydrogen-selective membranes and by removing CO₂ using the CaO reaction. Removing CO₂ is much more efficient due to the CO₂ amount being only 1/4 of the hydrogen amount, and the heat from the exothermic reaction of CaO with CO₂ provides the heat for the strong endothermic reaction

\[ CaO(s) + CO₂(g) \rightarrow CaCO₃(s); \nabla H = -178 kJ/mol \] (1)
Simulations and experimental evidence demonstrate that a rapid reaction of CaO with CO2 decreases the CO2 content and, therefore, enhances the endothermic steam methane reforming reaction. A high methane conversion and over 95% hydrogen content can be obtained. The use of the CaO reaction to capture CO2 to break the thermodynamic equilibrium limit requires CaO to be regenerated from CaCO3. This regenerated CaO can then be used in the reactor to enhance the steam reforming reaction. Therefore, a reactor-regenerator system is required: the reactor is required for steam reforming and the CaO reaction with the CO2, while the regenerator is required for regenerating CaO from CaCO3 and recycling it to the reactor. A circulating fluidized-bed reactor regenerator is suitable for this requirement (as in modern FCC units), in which the reactor is usually the riser and the regenerator is usually the downer. This situation requires a fast reaction between CaO and CO2 in the reactor (because of the short residence time due to the fast fluidization) and, similarly, a fast regeneration of CaCO3 in the regenerator. In addition, recent studies have described a circulating fluidized-bed reactor regenerator technology for post-combustion to remove CO2 from fuel gas using CaO-based sorbents. The need for a fast reaction of CaO with CO2 is a key technique.

Bhatia found that the gas–solid reaction of CaO with CO2 experiences a rapid reaction of CO2 followed by a slow CO2 diffusion-controlled reaction through the CaCO3 layer. A previous study on a nano-CaO reaction with CO2 also showed that the rapid reaction regime is followed by a slow reaction regime. Nano-CaO reacts rapidly with CO2, as shown in previous studies. The stability of using nano-CaO-based CaO sorbents was also experimentally studied by Florin and Lu. From the experimental studies, one significant difference between the nano-CaO and micro-CaO reaction with CO2 is that nano-CaO has much more surface area. Up to 80% of the conversion ratio occurs in the rapid surface reaction regime (within 2 minutes) for nano-CaO. Alternatively, the micro-CaO reaction with CO2 only contributes 20% of the conversion ratio in the rapid surface reaction regime. However, the reaction kinetics of the nano-CaO reaction with CO2 have not been quantitatively studied yet. Thus, the study of the fast surface reaction kinetics of CaO with CO2 is significant.

Many investigations considered the use of CaO obtained from the calcinations of natural minerals, such as limestone and dolomite, for carbonation through the reaction of CaO with CO2. CaCO3 exists in limestone and dolomite in micrometer-sized particles, and CaO particles of micrometer size are obtained after calcination. Therefore, almost all the models describe the reaction of CaO with CO2 based on the micro-CaO reaction with CO2 for a rapid surface reaction regime and a slow diffusion-controlled reaction regime. One of the classical models is the shrinking core model as shown in Eqs. 2 and 3 where X is the CaO conversion, K is the reaction rate constant (expressed by the Arrhenius equation), CCO2 is the concentration of CO2, \( \rho \) is the density of a CaO particle, R is the radius of a CaO particle, and D is the diffusion coefficient. Based on the simplicity of the shrinking core model, Johnsen utilized the effective diffusion and the external mass-transfer coefficient to modify the model based on their SEM/EDS observations. Because the CaO–CO2 reaction is sensitive to the pore-size distribution of calcines, Sun developed a new gas–solid reaction model based on discrete pore-size distribution measurements and applied it to the carbonation reaction of CaO to capture CO2. Sun suggested that the model accurately showed the pore-size distribution evolution and was easier to understand than other distributed-pore-based pore models. However, it is difficult to use because it requires the initial pore-size distribution of the CaO sorbent after calcination.

Another widely used pore model is the random pore model which assumes the pore structure is a network of randomly interconnected pores and can be represented as follows:

Chemical reaction control regime

\[
\frac{dX}{dt} = \frac{KC_{CO2}S_0(1-X)}{1-i_0} \sqrt{1-\psi \ln(1-X)}
\]

Diffusion control regime

\[
\frac{dX}{dt} = \frac{KC_{CO2}S_0(1-X)}{(1-i_0)\left[1 + \frac{D}{\rho R_0(1-\psi \ln(1-X))} \right]} \]

In Eqs. 4 and 5, \( K \) is the rate constant (expressed by Arrhenius equation), \( C_{CO2} \) is the concentration of CO2, \( S_0 \) is the initial total area per unit volume, \( i_0 \) is the porosity, and \( L_0 \) represents the initial total pore length in the porous system per unit volume. \( \psi \) is a structural parameter.

The disadvantages of this method are the complexity and the need to obtain information about the structural parameters. The models discussed above have been improved considerably by incorporating more details and properties of the adsorbents. However, they still fail to describe the kinetics of nano-CaO reactions with CO2, especially for the rapid reaction regime.

Based on previous experimental results of nano-CaO reactions with CO2 and a typical sigmoid-type conversion curve, author empirically used a Boltzmann equation to fit the curves in the rapid reaction regime and obtained good simulation results. No mechanism or model has described this feature during the initial nano-CaO carbonation reactions.

To establish a model of nano-CaO reactions with CO2, we recently proposed an ion migration mechanism that was useful in explaining the diffusion of CO2 in the CaCO3 layer formed. Bhatia proposed that Ca\(^{2+}\) and CO\(_3^{2-}\) ions are predominant in CaCO3 and that CO\(_2\) is the mobile species in ionic conduction through CaCO3. Furthermore, they
postulated that O\(^{-2}\) serves as a counter-current of a negatively charged species during the reaction process to maintain electroneutrality in the CaCO\(_3\) product layer. The reaction, diffusion and movement actions are described in Eqs. 6–8

At the pore surface: \(\text{CO}_2(g) \leftrightarrow (\text{CO}_2)_{\text{ads}}\) \hspace{1cm} (6)

\((\text{CO}_2)_{\text{ads}} + \text{O}^{-2} \rightarrow \text{CO}_3^{2-}\) \hspace{1cm} (7)

At the CaO – CaCO\(_3\) interface: \(\text{CO}_3^{2-} + \text{CaO} = \text{CaCO}_3 + \text{O}^{-2}\) \hspace{1cm} (8)

Haul et al.\(^{28,29}\) proposed that an isotopic exchange occurs between carbon dioxide and calcium carbonate. Yi et al.\(^{30}\) chose to use mono-, bi-, and tri-metal oxides that possess oxygen vacancies as an additive of the CO\(_2\) sorbent to provide a CO\(_2\) diffusion pathway and facilitate O\(^{-2}\) ion migration.

In this study, a condition to distinguish between a rapid reaction regime and a slow reaction regime is proposed. Then, based on the ion migration hypotheses, a new ion reaction mechanism is proposed, and a kinetic model is developed for the rapid surface reaction of nano-CaO with CO\(_2\). Finally, experiments were performed on the carbonation reaction of a sorption complex catalyst to examine and evaluate the kinetic model.

**Model development**

Based on the ion migration mechanism of CO\(_2\) and CO\(_3^{2-}\) shown in Eqs. 6 and 7, the sorption of CO\(_2\) is random on the surface of nano-CaO. The adsorption process may be described by an isothermal adsorption equation,\(^{31,32}\) which is independent of the reaction conversion; thus, we proposed two hypotheses.

1. Bhatia\(^{31}\) proposed that the formation and decomposition of CO\(_3^{2-}\) with O\(^{-2}\) was a possible pathway for effective CO\(_2\) diffusion. Hence, we proposed that the formation and decomposition of CO\(_3^{2-}\) reaches equilibrium through the movement of CO\(_3^{2-}\) during the reactions and is described by Eq. 10.

2. Due to the stability of CaO, the reaction formation of CaO is a solid, while O\(^{-2}\) is the counter-current motion and is derived from the decomposition or the carbonation reaction.

We propose a new ion reaction mechanism of nano-CaO with CO\(_2\) as presented in Eqs. 9–11.

Adsorption on the surface: \(\text{CO}_2(g) \leftrightarrow (\text{CO}_2)_{\text{ads}}\) \hspace{1cm} (9)

\((\text{CO}_2)_{\text{ads}} + \text{O}^{-2} \xrightleftharpoons[k_2]{k_1} \text{CO}_3^{2-}\) \hspace{1cm} (10)

Irreversible reaction : \(\text{CO}_3^{2-} + \text{CaO} \xrightarrow{k_3} \text{CaCO}_3 + \text{O}^{-2}\) \hspace{1cm} (11)

In the experiments conducted in this research, the CO\(_2\) concentration was far from the equilibrium concentration; thus, we speculate the carbonation reaction, Eq. 11, is irreversible. In the first stage, the initial product layer is small, and CO\(_2\) has an extremely high diffusivity, causing the reaction at the CaO-CaCO\(_3\) interface to be the control step.\(^{24}\) Hence, we assume that Eq. 11 is the controlling reaction. From the derivation of the reaction kinetics, an elementary reaction assumption is used. Thus, the reaction kinetics equation of nano-CaO reacting with CO\(_2\) is given by the following

\[ r = k_3 \times \theta_{\text{CO}_3^{2-}} \times \theta_{\text{CaO}} \] \hspace{1cm} (12)

From Eq. 12, \(k_3\) is the kinetic rate constant from Eq. 11, \(\theta_{\text{CaO}}\) is the active CaO ratio on the catalyst surface and \(\theta_{\text{CO}_3^{2-}}\) is the coverage ratio of CO\(_3^{2-}\) on the surface of the catalyst.

As expressed in hypothesis (1), because Eq. 10 reaches equilibrium and is an elementary reaction, it leads to Eq. 13

\[ k_1 \times \theta_{(\text{CO}_2)_{\text{ads}}} \times \theta_{\text{O}^{-2}} = k_2 \times \theta_{\text{CO}_3^{2-}} \] \hspace{1cm} (13)

where \(k_1\) and \(k_2\) are the forward and reverse kinetic rate constants from Eq. 10, respectively, \(\theta_{\text{O}^{-2}}\) is the coverage ratio of O\(^{-2}\) on the surface of the catalyst and \(\theta_{(\text{CO}_2)_{\text{ads}}}\) is the adsorption ratio of CO\(_2\) on the surface of the catalyst.

By combining Eqs. 12 and 13, and defining \(k' = \frac{k_3 \times k_4}{k_2}\), we obtain

\[ r = k' \times \theta_{(\text{CO}_2)_{\text{ads}}} \times \theta_{\text{CaO}} \times \theta_{\text{O}^{-2}} \] \hspace{1cm} (14)

From Eq. 14, \(\theta_{(\text{CO}_2)_{\text{ads}}}\) presents the isothermal adsorption behavior of CO\(_2\) from Eq. 9, which can be obtained by the Langmuir, Temkin, or Freundich isothermal adsorption equations. In this study, the Temkin isothermal adsorption equation is more suitable to describe the chemical adsorption characteristics of CaO and CO\(_2\) because of the exponential relationship between the adsorption active energy and adsorption capacity. This relationship can be expressed as follows

\[ \theta_{(\text{CO}_2)_{\text{ads}}} = b \times \ln(a \times P) \] \hspace{1cm} (15)

where \(a\) is a function of temperature, \(b\) is a constant and \(\theta_{(\text{CO}_2)_{\text{ads}}}\) is the coverage ratio of CO\(_2\) on the surface of CaO.

The variables \(\theta_{\text{O}^{-2}}\) and \(\theta_{\text{CaO}}\) can be obtained by simplifying the ion migration hypothesis. Based on hypothesis (1), we assume that the mole number of O\(^{-2}\) in the sorbent is proportional to the mole number of CO\(_3^{2-}\) ions or CaCO\(_3\) formed. For the local reaction area, if we set the mole number of reacted CaO as \(N_1\), the mole number of unreacted active sites of CaO on the surface as \(N_2\), the total CaO mole number on the surface as \(N\), and the mole number of O\(^{-2}\) ions is proportional to the number of reacted CaO, where \(C\) is proposed as the proportionality coefficient, a constant, then we obtain the following equations

\[ N_1 + N_2 = N \] \hspace{1cm} (16)

Hence

\[ \theta_{\text{O}^{-2}} = \frac{CN_1}{N} \] \hspace{1cm} (17)

\[ \theta_{\text{CaO}} = \frac{N_2}{N} \] \hspace{1cm} (18)

For the adsorbent, if we assume that \(n\) is the mole number of CaO in the sorbent, \(X\) is the conversion of CaO, and \(X_a\) is the ultimate conversion of CaO in the rapid reaction regime, then the conversion \(X\) and \(X_a\) can be expressed as follows

1572 DOI 10.1002/aic Published on behalf of the AIChE May 2012 Vol. 58, No. 5 AIChE Journal
Substituting Eqs. 16–20 in Eq. 14, we can express the rate as Eq. 21

\[ r = k' \times C \times \theta_{(CO_2)_{ads}} \times \frac{X}{X_u} \left( 1 - \frac{X}{X_u} \right) \]  

(21)

The reaction rate can also be expressed as Eq. 22

\[ r_1 = \frac{dN_1}{dt} \]  

(22)

Introducing Eq. 19 in Eq. 22, we obtain Eq. 23

\[ r_1 = n \frac{dX}{dt} \]  

(23)

\[ n \] is a constant in a reaction; therefore, we obtain a varied type of the reaction rate

\[ r = \frac{dX}{dt} \]  

(24)

Thus, \( r = \frac{dX}{dt} = k \times \frac{X}{X_u} \left( 1 - \frac{X}{X_u} \right) \)  

(25)

where

\[ k = k' C \theta_{(CO_2)_{ads}} \]  

(26)

The differential equation expressed in Eq. 25 is as follows

\[ \frac{dr}{dt} = \frac{d^2X}{dt^2} = \frac{k}{X_u^2} (X_u - 2X) \frac{dX}{dt} \]  

(27)

When \( \frac{d^2r}{dt^2} = \frac{d^2X}{dt^2} = 0 \), it is related to the point of \( r_{\text{max}} \); we define this related conversion point as \( X_1 \), and we obtain \( X_1 = 1/2X_u \).

From Eqs. 25 and 27, the reaction rate variation with time is nonmonotonic and reaches a maximum \( (r_{\text{max}}) \) when the conversion \( X \) is half of the ultimate conversion \( X_u \) in the chemical reaction control regime. The experimental results of the two curves are shown in Figure 1: the conversion \( X \) vs. the time \( t \) curve (the dashed curve) and the reaction rate \( dX/dt \) vs. \( t \) curve (the solid curve). The left vertical axis represents the reaction conversion \( X \), and the right vertical axis represents the reaction rate \( dX/dt \). There is a maximum reaction rate, \( r_{\text{max}} \), determined by the point of \( d^2X/dt^2 = 0 \), and related to the conversion \( X_1 \). When we obtain the conversion \( X_1 \), we can calculate the ultimate conversion \( X_u \). Furthermore, we proposed a criterion when the conversion point of \( X \) increased to \( X_u \), as shown in Figure 1. \( X_u \) is the critical point that divides the reaction into a rapid reaction regime and a slow reaction regime. When \( X \leq X_u \), the reaction is a rapid reaction regime, and when \( X > X_u \), it is a slow reaction regime.

From Figure 1, we define the time with the point of \( dX/dt = 0 \) or \( X_1 = X_u/2 \) as \( t_0 \). Using the initial conditions below and integrating Eq. 25 for the area of \([0, t_0]\) and \([t_0, t]\), we obtain the final integral equation

\[ 0 < t \leq t_0 : t = t, \quad X = X \]  

\[ t = t_0, \quad X = X_1 = 1/2X_u \]  

\[ t_0 < t : t = t_0, \quad X = X_1 = 1/2X_u \]  

\[ t = t, \quad X = X \]  

\[ X = X_u - \frac{X_u}{1 + \exp \left[ \frac{(t-t_0)k}{X_u} \right]} \]  

(0 \leq X \leq X_u)  

(28)

Equation 28 is very similar to the Boltzmann equation and represents sigmoid-type conversion curves. When \( t < t_0 \), \( dX/dt \) increases; however, when \( t > t_0 \), \( dX/dt \) decreases with increasing time. When \( X > X_u \), the reaction enters the slow reaction regime. The layer of CaCO3 formed by rapid carbonation dominates the carbonation rate. The kinetics of the slow reaction section is the same as other models for micro-CaO reacting with CO2.

The reason for the sigmoid-type conversion curves in the rapid surface reaction regime shown in Figure 1 is the diffusion rate of CO2 and the amount of unreacted nano-CaO. The process can be explained by the ion reaction mechanism of Eqs. 10 and 11. At the beginning of the reaction, the diffusion rate of CO2 in the gas phase is fast, and much of the CO2 forms according to Eq. 10. This process simultaneously accelerates the CaO carbonation reaction of Eq. 11 to form CaCO3. After a short reaction time, the conversion rate is lower because the amount of unreacted nano-CaO is decreased. A layer of CaCO3 may not form during the rapid surface reaction regime. After a layer of CaCO3 is formed, CO2 diffusion through the CaCO3 becomes the rate-limiting step. The mechanism and model for CO2 diffusion is similar to the micro-CaO reaction with CO2, which is not addressed in this article.

**Experimental**

To evaluate the model, a sorption complex catalyst, containing nano-CaO as the CO2 adsorbent and Ni as the
reforming catalyst, was prepared. Nano-CaCO₃ powder with a particle size of 70 nm (Huzhou Linghua, China) was used as the nano-CaO precursor. The content of nano-CaCO₃ in the complex was ~50%.

A thermogravimetric analyzer (PyrisITGA, Perkin–Elmer) was used to study the carbonation reaction kinetics of nano-CaO reacting with CO₂ in the sorption complex catalyst. Approximately 3 mg of catalyst complex was used in the sample holder to avoid interparticle diffusion effects in the platinum basket. The complex was calcined for 10 min at 1003 K in a N₂ atmosphere with a gas flow rate of 46 ml/min. The temperature was then decreased to the designated reactive temperature, and CO₂ gas was introduced to obtain an atmosphere with the designed CO₂ partial pressure. The carbonation reaction was studied over a temperature range of 773–873 K, and the CO₂ partial pressure

\[ P_{\text{CO}_2} \] was varied between 0.012 and 0.020 MPa. Based on the CO₂ content of normal industrial applications, we selected a CO₂ partial pressure of 0.012, 0.014, 0.016, or 0.020 MPa. The carrier gas was nitrogen. The reasons for selecting this range of reaction temperatures and CO₂ partial pressures were the industrial need and the results of previous studies.

**Experimental results and discussions**

Figures 2–5 show the carbonation conversions of the nano-CaO in the sorption complex catalyst with time under the partial pressures of CO₂ of 0.012, 0.014, 0.016, and 0.020 MPa at the different temperatures of 773, 823, and 873 K, respectively. The carbonation conversion, \( X \), of nano-CaO varied with the temperature and CO₂ partial pressure.

![Figure 2. Conversion of nano-CaO carbonation in the sorption complex catalyst.](image)
The carbonation temperatures were 773, 823, and 873 K, respectively, and the \( P_{\text{CO}_2} \) was 0.012 MPa.

![Figure 3. Conversion of nano-CaO carbonation in the sorption complex catalyst.](image)
The carbonation temperatures were 773, 823, and 873 K, respectively, and the \( P_{\text{CO}_2} \) was 0.014 MPa.

![Figure 4. Conversion of nano-CaO carbonation in the sorption complex catalyst.](image)
The carbonation temperatures were 773, 823, and 873 K, respectively, and the \( P_{\text{CO}_2} \) was 0.016 MPa.

![Figure 5. Conversion of nano-CaO carbonation in the sorption complex catalyst.](image)
The carbonation temperatures were 773, 823, and 873 K, respectively, and the \( P_{\text{CO}_2} \) was 0.020 MPa.
The curves represent typical sigmoid curves, similar to nano-CaO reactions with CO₂ in CaO/Al₂O₃ sorbents described in other published work related to the carbonation reaction. Fig. 6 and 7 show the sigmoid X vs. t curves and the nonmonotonic r (dX/dt) vs. t curves at the first 2 minutes of the fast reaction sections for different temperatures and CO₂ partial pressures. The left coordinate axis represents the reaction conversion X, and the right axis represents the reaction rate r (dX/dt). From Figures 6 and 7, sigmoid-type curves are obvious, and each curve appears to be a peak. Each peak relates to an r max point, and the sigmoid-shaped curves relate to the X curve in Figures 6 and 7. Figure 6 shows that as temperature increased, both t₀ and r max increased. The reaction rate at 873 K was higher than that at the other two temperatures. Figure 7 shows that as the carbonation rate increased and the reaction time (t₀) increased, the CO₂ partial pressure also increased.

**Table 1. The Vales of X_u Under the Various Conditions**

<table>
<thead>
<tr>
<th>P_CO₂ (MPa)</th>
<th>773 K</th>
<th>823 K</th>
<th>873 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.020</td>
<td>21.90</td>
<td>34.16</td>
<td>41.28</td>
</tr>
<tr>
<td>0.016</td>
<td>21.80</td>
<td>33.89</td>
<td>40.86</td>
</tr>
<tr>
<td>0.014</td>
<td>22.00</td>
<td>33.51</td>
<td>39.31</td>
</tr>
<tr>
<td>0.012</td>
<td>22.05</td>
<td>32.02</td>
<td>38.71</td>
</tr>
</tbody>
</table>

The variables X_u, t₀, and k in Eq. 28 change with the reaction temperature or CO₂ partial pressures. The results from Figures 2–5 of the carbonation conversion were fitted using Origin software to determine the parameters X_u, t₀, and k.

**Estimation of X_u**

From the experimental results shown in the Table 1, the ultimate conversion of the rapid reaction regime, X_u, was found to be first order with respect to the reaction temperature (773–873 K). Thus, a linear equation, Eq. 29, was used to empirically express X_u for CaO carbonation reaction

\[
X_u = -118.09 + 0.18T \quad (773. K \leq T \leq 873. K) \tag{29}
\]

Similar methods were used in the empirical carbonation conversion equations. Li also found that the ultimate conversion of CaO was independent of the CO₂ fraction but increased linearly with increasing reaction temperatures (873–973 K). Lee proposed that the total ultimate conversion be expressed as a function of k, which is a kinetic rate constant.

Apparently, a higher temperature promotes the reaction of CaO with CO₂ resulting in a higher ultimate conversion during the kinetically-controlled reaction regime. Higher temperatures may also accelerate the diffusion of the CO₃²⁻ and O²⁻ ions in the CaCO₃ layer. This phenomenon is supported by Alvarez and Abanades, who showed that the critical thickness of the product layer affected the apparent ultimate conversion. In addition, higher temperatures promoted the endothermic reaction of CaO carbonation.

**Estimation of t₀**

Figures 6 and 7 show that an increase in the partial pressure of CO₂ in the atmosphere or a decrease in the reaction temperature has the same effect as decreasing the time required to reach the maximum reaction rate t₀. However, the higher partial pressure of CO₂ caused an increase in the amount of CaO conversion, and lower reaction temperatures caused a decreased conversion. Increasing the CO₂ partial pressure increased the CO₂ equilibrium adsorption amount, and increasing the temperature should promote the endothermic reaction of CaO with CO₂. Thus, both temperature and CO₂ partial pressure were used to estimate t₀ using the least square method, as shown empirically in Eq. 30

\[
t₀ = -0.57 + 0.297T/100 - 58.16P_{CO₂} \tag{30}
\]

The unit of the reaction temperature T is K, and the unit of the CO₂ partial pressure, P_{CO₂}, is MPa. Equation 30 is valid when 773 K ≤ T ≤ 873 K and 0.012 MPa ≤ P_{CO₂} ≤ 0.02 MPa.
Estimation of $k$

The Temkin isothermal adsorption equation was introduced in Eq. 26. The constant $b$ is a temperature-independent constant. Using this constant, Eq. 31 was derived

$$k = k_4 \times \ln(a \times P_{CO_2})$$

In this equation, $k_4 = k' C_b$, where $C$ and $b$ are independent of temperature.

An Arrhenius plot was constructed for individual values of $k_4$ obtained from the fitted result at various temperatures. The value of the activation energy $E$ was 30.2 kJ/mol, and $k_4$ was obtained using Eq. 32

$$k_4 = 11.5723 \times 10^3 \times \exp \left( -\frac{30.2 \times 10^3}{8.314T} \right)$$

Although the constant decreased steadily as the temperature increased, the relationship between the parameter, $a$, and the temperature, $T$, was not suitable for the Arrhenius equation. As a result, an empirical equation was derived

$$a = -444.13 + 1.17T - 7.39 \times \left( \frac{T}{100} \right)^2$$

Based on the discussion above, the effects of $k$ can be characterized as either the kinetic reaction rate or the CO$_2$ adsorption capacity. This contradictory relationship weakened the influence of temperature on the apparent reaction rate. In some cases, including those presented by Bhatia, Li, and Dennis, temperature did not affect the apparent reaction rate.

Temperature may affect the kinetic constant in the Arrhenius equation; however, higher temperatures could lead to more active CaO, as discussed in sections above. The equilibrium adsorption amount decreased, and as a result, the negative effect of high temperature on the equilibrium adsorption amount made the apparent kinetic constant, $k_4$, irregular with regard to temperature in the Arrhenius equation.

Thus, the rapid carbonation kinetic model of nano-CaO in the sorption complex catalyst is presented as

$$X = X_a - \frac{X_u}{1 + \exp \left( \frac{t-T_0}{a+b} \right)}$$

where, $X_u = -118.09 + 0.18T$

$$t_0 = -0.57 + 0.29T/100 - 58.16P_{CO_2}$$

$$k = 11.572 \times 10^3 \times \exp \left( -\frac{30.2 \times 10^3}{8.314T} \right) \times \ln(a \times P_{CO_2})$$

$$a = -444.13 + 1.17T - 7.39 \times \left( \frac{T}{100} \right)^2$$

(773 K $\leq T \leq 873$ K, 0.012 MPa $\leq P_{CO_2} \leq 0.02$ MPa).

Model examination

Figure 8 shows a comparison of the predicted and the experimental data in the kinetically controlled region from the carbonation conversions derived from Eq. 28. The average relative deviation was less than 9.86% when the carbonation conversion was greater than 3%. When the conversion was less than 3%, the average value of the absolute errors was 0.77%, and the maximum of the absolute error was 1.83%. It appears that the kinetic model derived in this article accurately depicts the carbonation kinetics of a sorption complex catalyst. Furthermore, the $X$-$t$ sigmoid-type curve of nano-CaO reactions with CO$_2$ can be represented by the kinetic model in Eq. 28.

Conclusions

Based on the hypotheses of ion migration, a new ion reaction mechanism of nano-CaO reacting with CO$_2$ has been proposed. A new condition to distinguish between rapid surface reactions and slow diffusion reactions of nano-CaO with CO$_2$ was proposed. A kinetic model in the form of the Boltzman equation was developed for the first time. The kinetic model is in agreement with the characteristics of the carbonation reaction of nano-CaO with CO$_2$ in the kinetically controlled reaction regime. The experimental carbonation reaction curves were successfully described by the kinetic model of a sorption complex catalyst at temperatures of 773–873 K and CO$_2$ partial pressures of 0.012 and 0.020 MPa. The activation energy during carbonation was estimated to be 30.2 kJ/mol. The average relative deviation of carbonation in the rapid kinetic control reaction regime was less than 9.8%.

Acknowledgments

The authors are grateful to the National Natural Science Foundation of China (20876142) and to the China High technology ministry 863 program (2009AA05Z104) for financial support.

Notation

- $a$ = parameter in the Temkin isothermal adsorption equation
- $b$ = constant in the Temkin isothermal adsorption equation
- $C$ = proportional coefficient, a constant
- $C_{CO_2}$ = concentration of CO$_2$
- $D$ = diffusion coefficient
- $E$ = activation energy
- $k$ = kinetic rate constant in Eq. 28

Figure 8. Comparisons of predicted and experimental data for carbonation conversion.
\[ k_1 \text{ and } k_2 = \text{kinetic rate constants of the reaction in Eq. 11} \]
\[ k_3 = \text{kinetic rate constant of the reaction in Eq. 12} \]
\[ k_4 = \text{parameter in Eq. 31} \]
\[ k' = \text{effective kinetic rate constant in Eq. 15} \]
\[ K = \text{kinetic rate constant in Eqs. 2, 4, and 5} \]
\[ L_0 = \text{initial total pore length in the porous system per unit of volume} \]
\[ n = \text{mole number of CaO in the sorbent} \]
\[ N = \text{mole number of the total CaO on the surface} \]
\[ N_{1i} = \text{mole number of reacted CaO on the surface} \]
\[ N_{2i} = \text{number of unreacted active sites of CaO on the surface} \]
\[ P_{CO_2} = \text{partial pressure of CO}_2 \text{ in the reaction atmosphere} \]
\[ S_0 = \text{initial surface area per unit volume} \]
\[ t = \text{carbonation reaction time} \]
\[ t_0 = \text{reaction time related to the maximum conversion rate} \]
\[ T = \text{reaction temperature} \]
\[ X = \text{conversion of CaO} \]
\[ X_i = \text{conversion of CaO related to the maximum conversion rate} \]
\[ X_u = \text{ultimate conversion of CaO in the rapid reaction region} \]

Greek letters
\[ \alpha_0 = \text{initial porosity} \]
\[ \theta_{\text{CO}_2,\text{ads}} = \text{coverage ratio of CO}_2 \text{ on the surface of CaO} \]
\[ \theta_{O^2-} = \text{coverage ratio of O}^2^- \text{ on the surface of the catalyst} \]
\[ \theta_{\text{CO}_2} = \text{coverage ratio of CO}_2^- \text{ on the surface of the catalyst} \]
\[ \theta_{\text{CaO}} = \text{active CaO ratio on the catalyst surface} \]
\[ \psi = \text{structural parameter} \]

Literature Cited

*Manuscript received Oct. 20, 2010, revision received Feb. 3, 2011, and final revision received May 2, 2011.*