Effect of calcium and barium on potassium-catalyzed gasification of ash-free carbon black

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Abstract

Gasification of carbon black, an ash-free carbon feed, was performed with K_2CO_3 and either $CaCO_3$ or $BaCO_3$ as catalysts to examine their interaction. Mixtures were prepared by low-energy ball-milling, and then gasified with CO_2 at 750-850 °C in a thermogravimetric analyzer. At temperatures below 800 °C, the presence of calcium had little impact on the potassium-catalyzed gasification of carbon black. At higher temperatures, calcium promoted the activity of potassium up to ~50 % conversion through the formation of a eutectic phase that increased the diffusivity of the potassium. At higher conversions, the tendency of $CaCO_3$ to sinter and limit diffusion of CO_2 to the carbon inhibited the reaction. $BaCO_3$ also formed a eutectic phase with K_2CO_3 confirming that the phase change was beneficial. In contrast to $CaCO_3$, however, $BaCO_3$ does not sinter at 850 °C, such that gasification was promoted to complete conversion.

Keywords

gasification; potassium; calcium; eutectic; carbon; carbon black; catalysis

1. Introduction

Gasification is a technique for conversion of carbon feeds to usable fuels such as H_2 , CO , and CH_4 , and is of particular interest for feeds where the by-products emitted from combustion are of concern, such as coal [1-6] or bio-wastes [7-9]. Metallic species in the feed materials, including calcium and potassium, can be used as intrinsic gasification catalysts [10-14]. Calcium can be found in feeds such as biosolids/sewage sludge [15-18], coal [19-22], and biomass [10, 23, 24], while potassium is found in biomass with an order of magnitude higher abundance than typically found in coal [23, 25] or biosolids [26, 27]. Biomass has been co-gasified with coal to increase the reaction rate by introducing more potassium [27-32]. The higher diffusivity (or mobility) of potassium compared to calcium during gasification has been used in the literature to explain why potassium is a more active gasification catalyst [33-39]. Barium is more active as a gasification catalyst than calcium, but still leads to reaction rates an order of magnitude lower than the rates observed with potassium [40]. Published studies which use barium as a gasification catalyst are from 1993 or earlier [41-48], with recent studies focusing on using barium compounds as catalyst supports for downstream syngas processing [49, 50] or as oxygen carriers for chemical-looping gasification [51, 52]. Barium is studied far less frequently than calcium because barium is less abundant in gasification feeds; for example, one study found calcium to be 50-100 times more abundant than barium on a weight basis when sampling sewage sludge from different European countries [53].

Calcium has been reported to have a synergistic effect with potassium for the gasification of coal char and graphite [54-57]. Wang et al. proposed that a bimetallic carbonate compound formed during gasification when both potassium and calcium salts are present [54]. In our previous study [26], XRD analysis of the remaining ash after CO_2 gasification at 850 °C of carbon black with

added KOH and Ca(OH)_2 did not provide evidence for this bimetallic compound. There was, however, evidence of calcium preferentially reacting with aluminum and silicon to form aluminosilicate compounds, to allow the potassium to remain in a catalytically active form. In addition, the initial gasification rate for carbon black (i.e., gasification in the absence of deactivating aluminosilicates) was higher in the presence of calcium.

Wang et al. have proposed that calcium could also promote potassium through the formation of a low-melting point eutectic [54]. They suggested that the eutectic formation increased the reaction rate by enhancing the formation of the K-char complex that is required for catalytic gasification. During heating, the precursors decompose into forms which are more mobile and effective as catalysts. For example, K_2CO_3 is less effective as a gasification catalyst when heated in CO_2 than when heated in N_2 , because CO_2 inhibits the decomposition of K_2CO_3 to K [58]. The composition within a gasifier will be complex and phase diagrams for these mixtures are not available. Several studies, however, have demonstrated the formation of eutectic mixtures by measuring the ash sintering temperature. For example, Zhang et al. [59] found that the ash sintering temperature of lignite coal decreased from $\sim 860^\circ\text{C}$ to $\sim 520^\circ\text{C}$ when K_2CO_3 and CaCO_3 , were added.

The current study was undertaken to better understand the interaction between potassium and calcium during gasification. The preliminary results suggested that eutectic formation may influence the behaviour at different temperatures ($750\text{--}850^\circ\text{C}$). Barium, which also forms a eutectic mixture with potassium, was used in some experiments. The gasification was performed in a thermogravimetric analysis unit and characterization was performed using differential scanning calorimetry and scanning electron microscopy with energy dispersive X-ray analysis.

2. Materials & Methods

2.1 Sample preparation

Carbon black (CB, Cabot Monarch 120, Cabot Corp, Boston, MA) was the carbon feed. Proximate analysis of the CB, performed by Loring Laboratories, Calgary, Alberta, Canada, found the fixed carbon content to be 99.2 wt.% (dry basis), the ash content to be 0.6 wt.%, and the volatile content to be 0.2 wt.%. The ultimate analysis found carbon to be 99.4 wt.% (dry ash-free basis), and no other elements were found in either the ultimate or ash analysis. The CB was mixed with different amounts of CaCO_3 , K_2CO_3 and/or BaCO_3 (Sigma-Aldrich, St. Louis, MI). In our earlier work, hydroxides were selected as catalyst precursors [26]. The decomposition of KOH was found to occur in the same temperature range as the calcium-potassium eutectic formation reported in the literature [54], so carbonates were chosen to avoid confounding of these two occurrences. KOH and K_2CO_3 are reported to have similar catalytic activity for gasification, and to be higher than those of KNO_3 , KSO_4 , and KCl [60-62], so the selection of carbonates ensured a high rate of gasification. Samples were ball-milled for 24 h in a low-energy rotary tumbler (model 33B, Lortone, Mukilteo, WA) with zirconia balls 5 mm in diameter. In all mixtures, the atomic ratio of each metallic element (M) to carbon was 0.1, unless otherwise stated. Samples contained one metal - Ca or K - or two metals - Ca and K, or Ba and K - and were named according to the metal precursors. For example, sample CB- K_2CO_3 had a K:C ratio of 0.1, while sample CB- K_2CO_3 - CaCO_3 had a K:C ratio of 0.1 and a Ca:C ratio of 0.1. For a few experiments, catalyst to carbon ratios of 0.05 and 0.01 were used and these ratios have been explicitly stated on the appropriate figures.

2.2 Gasification

During gasification, both thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) results were obtained using a simultaneous DSC/TGA (SDT, TA Instruments SDT Q600, New Castle, DE), monitoring both the heat flow and mass. In each experiment, 3.5 mg of sample was heated in flowing nitrogen (200 mL/min) at 20 °C/min to the desired temperature (750 °C, 775 °C, 800 °C, 825 °C, or 850 °C), and then CO₂ (200 mL/min) was introduced as the gasification agent, with the nitrogen flow reduced to 5 mL/min. This minimal flow of nitrogen prevented backflow of the CO₂ over the TGA balance, ensuring accurate weight readings. Conversion, X , was calculated using the following equation:

$$X_t = \frac{m_0 - m_t}{m_0 - m_f} \quad (1)$$

where m denotes mass, and the subscripts 0, t , and f denote the initial value, the value at time t , and the final value, respectively. The rates of reaction were calculated using numerical integration:

$$\text{rate}(t_1) = \frac{dX}{dt}(t_1) = \frac{X_{t_2} - X_{t_1}}{t_2 - t_1} \quad (2)$$

where the subscripts 1 and 2 denote two consecutive time points. 50 data points were collected per minute.

The effective activation energy for different sample mixtures was calculated according to the isoconversional method for integral data collected isothermally (e.g., TGA data at a constant temperature), recommended by the International Confederation for Thermal Analysis and Calorimetry [63]. In this method, the variable $g(\alpha)$ was used to denote the unknown solution to the integral of the Arrhenius equation:

$$g(\alpha) = A \int_0^t e^{-\frac{E_A}{RT}} dt = A e^{-\frac{E_A}{RT}} t \quad (\text{at const. } T) \quad (3)$$

where A is the pre-exponential factor, E_A is the effective activation energy, R is the universal gas constant, and T is the temperature. This equation can be rearranged as follows:

$$\ln(t) = \ln\left(\frac{g(\alpha)}{A}\right) + \frac{E_A}{RT} \quad (4)$$

In this form, plotting $\ln(t)$ against $1/T$ gives E_A/R as the slope. Because $g(\alpha)$ is unknown, the value of E_A cannot be determined without first linearizing the data.

The use of the isoconversional method meant the activation energy could be determined directly from the TGA data. Activation energy can also be determined from use of a gasification model, such as the random pore model [64] or the extended random pore model [65]. Use of a model requires assumption of a reaction order, but the reaction order changes with conversion [66]. The isoconversional method has been used in recent studies in the literature to determine activation energy for gasification [67, 68] because it does not require assumption of a reaction order.

The effective activation energy was calculated in conversion increments of 10% between 10% and 90%. Below 10% conversion, the error in the recorded time was significant, while above 90% conversion, the change in mass with time was so small that including these points would have disproportionately influenced the effective activation energy determination. For example, at 850 °C sample CB-K₂CO₃ required less than 0.5 min to reach 10% conversion, and reached 90% conversion in 5.7 min, but the mass continued to decrease up to 100 min.

2.3 Characterization

The melting and decomposition temperatures of the precursors were identified using DSC analysis. Both melting and decomposition are endothermic processes. For these measurements, 3.5 mg of K_2CO_3 , $CaCO_3$, and a mixture of K_2CO_3 and $CaCO_3$ (K:Ca atomic ratio of 1:1) were heated at 20 °C/min in CO_2 to prevent decomposition of $CaCO_3$ to CaO.

Scanning electron microscopy (SEM, Phenom ProX, Thermo-Fisher Scientific, Waltham, MA) with energy-dispersive X-ray spectroscopy (EDX) capability was used to determine particle sizes, morphologies, and composition. Samples were placed on double-sided carbon tape that was then placed on the SEM stage.

3. Results & Discussion

3.1 Calcium and potassium interaction at different temperatures

Carbon black was gasified with potassium (CB- K_2CO_3) or with potassium and calcium (CB- K_2CO_3 - $CaCO_3$) at temperatures between 750 °C and 850 °C and the rate versus conversion curves are shown in Fig. 1. For comparison, the maximum gasification rate of CB was 0.0017 min⁻¹, and of CB with only calcium (CB- $CaCO_3$) was 0.0085 min⁻¹ at 850 °C. As shown in Fig. 1, the rates were the same within experimental error whether or not calcium was present at both 750 °C and 775 °C. The rates were at least an order of magnitude higher when catalyzed by potassium than by calcium [26], demonstrating that the rate is determined by the potassium-catalyzed reaction pathway, and that there is likely no interaction between calcium and potassium.

At the higher temperatures, the gasification behaviour of the two samples was not the same. In the presence of calcium at 800 °C and 825 °C, the gasification rates were similar up to 40-50%

conversion and then lower than those with only potassium. At 850 °C, the curves cross at 50% with calcium promoting the reaction before 50% conversion and inhibiting the reaction from 50-100% conversion. The different behaviors for samples CB-K₂CO₃ and CB-K₂CO₃-CaCO₃ demonstrated that there was an interaction between the potassium and calcium, but the nature of the interaction depended on the temperature and the degree of conversion.

Fig. 1. CO₂ gasification rate versus conversion for CB with K₂CO₃ (solid lines) and CB with K₂CO₃ and CaCO₃ (dashed lines) at temperatures between 750 and 850 °C.

3.2 Eutectic formation

Literature results attributed the promoting effect of calcium on potassium in the absence of aluminosilicates to the formation of a eutectic phase [54], so this eutectic phase formation between potassium and calcium was explored further. The DSC results for K₂CO₃, CaCO₃ and a mixture (1:1 Ca:K molar ratio with no CB) are shown in Fig. 2. The DSC curve for K₂CO₃ contains an endothermic peak that corresponds to the melting point of 891 °C. In the DSC curve for CaCO₃, the broad endothermic peak between 900 °C and 970 °C corresponds to the decomposition of CaCO₃ to CaO and CO₂. The melting points of CaCO₃ and CaO are 1339 °C and 2572 °C, respectively. Decomposition of CaCO₃ was observed at approximately 725 °C for CB-CaCO₃ heated under nitrogen flow, but in a CO₂ atmosphere the decomposition occurred at a higher

temperature. The DSC curve for the K_2CO_3 - CaCO_3 mixture contained two peaks beginning at 822 °C and 917 °C, respectively. The peak at 822 °C corresponds to the eutectic phase formation. The peak at 917 °C was consistent with CaCO_3 decomposition, and contained a shoulder at the low temperature side. This shoulder corresponded with the K_2CO_3 melting point, suggesting that some K_2CO_3 had not melted at the lower temperature because the $\text{K}_2\text{CO}_3/\text{CaCO}_3$ ratio was too low to form a low-melting eutectic phase for all of the K_2CO_3 present. In Fig. 1, the promoting effect of calcium on potassium-catalyzed gasification was only observed at temperatures above 825 °C, which is consistent with a eutectic phase forming at 822 °C.

Fig. 2. DSC curves for K_2CO_3 , CaCO_3 , and a mixture of K_2CO_3 and CaCO_3 (K:Ca = 1:1, atomic basis). The samples were heated at 20 °C/min in flowing CO_2 (exothermic is positive).

Several mixtures of K_2CO_3 and CaCO_3 (1:1 K:Ca atomic ratio) were heated at 20 °C/min to 750 °C and 850 °C, as in the gasification experiments, before they were cooled to room temperature and then examined in the SEM (Fig. 3). Before heating, CaCO_3 was present as well-defined cubic crystals (~8 µm on one edge), while K_2CO_3 existed as irregular clusters (~20 µm in diameter) of smaller crystals (~1.5 µm in diameter), shown in Fig. 3a. Upon heating to 750 °C, the CaCO_3

particles remained as well-defined crystals, while the clusters of K_2CO_3 crystals became smaller (Fig. 3b), suggesting that some of the crystals had dispersed at the elevated temperature. There was no observed interaction between the two species. After heating to $850\text{ }^\circ\text{C}$, neither CaCO_3 nor K_2CO_3 crystals could be identified in the larger particles that were greater than $50\text{ }\mu\text{m}$ in size (Fig. 3c). The sample had to be chipped out of the crucible, which suggested the solidification of a liquid phase formed at the eutectic temperature of $822\text{ }^\circ\text{C}$.

Fig. 3. SEM of K_2CO_3 - CaCO_3 a) unheated, b) heated to $750\text{ }^\circ\text{C}$, and c) heated to $850\text{ }^\circ\text{C}$. Circles identify clusters of K_2CO_3 crystals. The scale bar in b) applies to all three images.

Similarly, in the SEM images of sample CB- K_2CO_3 - CaCO_3 after heating to $850\text{ }^\circ\text{C}$, there is evidence of solidification of a liquid phase (Fig. 4). Before heating (Fig. 4a), CaCO_3 and K_2CO_3 were dispersed with the CB, with the catalysts appearing as white crystals mixed with the gray CB (the CaCO_3 and K_2CO_3 particles were indistinguishable in the SEM images). The sample was heated to $850\text{ }^\circ\text{C}$ in N_2 , and then held under CO_2 flow for 10 s to allow CaCO_3 to reform from CaO (Fig. 4b). The cluster in Fig. 4b was much larger than any seen in the unheated mixture, and CaCO_3 and K_2CO_3 crystals were not evident. The surface of the particle was not smooth, suggesting that some gasification had occurred. The EDX analysis did not detect carbon, but only potassium and

calcium in a 1:1 molar ratio as well as oxygen (38% K, 37% Ca, 35% O), demonstrating that the CB was coated and that potassium was not significantly volatile at these conditions. After 80% conversion, the sample was stuck to the crucible and the particles in Fig. 4c are the broken pieces scraped out of the crucible. EDX analysis of these pieces detected only potassium and calcium in a 1:1 atomic ratio (51% Ca, 49% K).

Fig. 4. SEM images of CB-K₂CO₃-CaCO₃ mixture a) unheated, b) after heating to 850 °C and holding for 10 s under CO₂ flow, and c) after CO₂ gasification to 80% conversion. The scale bar in c) applies to all three images.

To further understand the role of eutectic formation, a similar experiment was performed using BaCO₃, instead of CaCO₃, added to CB-K₂CO₃. For the 1:1 molar ratio of these carbonates used in this experiment, the onset of eutectic melting occurs at 784 °C, and the entire mixture is liquid above ~847 °C [69]. The decomposition temperature of BaCO₃ is above 1000 °C in nitrogen flow [70]. As shown in Fig. 5, the addition of barium increased the gasification rate of CB-K₂CO₃, and, in contrast to the CB-K₂CO₃-CaCO₃ sample, the gasification rate was consistently higher to complete conversion.

Fig. 5. Conversion versus time for CO₂ gasification at 850 °C of CB with added potassium, calcium, and/or barium carbonates.

The BaCO₃ crystals were needle-shaped after ball-milling and can be identified in the mixture in Fig. 6a; the K₂CO₃ is indistinguishable from the CB. Upon heating to 850 °C (Fig. 6b), the particles agglomerated consistent with eutectic formation between BaCO₃ and K₂CO₃. The CB-K₂CO₃-BaCO₃ particles were smaller (10-40 μm, Fig. 6b) than those of CB-K₂CO₃-CaCO₃ (30-70 μm, Fig. 4b). After 80% conversion, the CB-K₂CO₃-BaCO₃ mixture was still present as a loose powder in the crucible, in contrast to the CB-K₂CO₃-CaCO₃ mixture that had to be scraped out of the crucible. In their respective SEM images at 80% conversion, CB-K₂CO₃-BaCO₃ was porous (Fig. 6c), while CB-K₂CO₃-CaCO₃ was non-porous (Fig. 4c).

Fig. 6. SEM images of CB-K₂CO₃-BaCO₃ mixtures a) unheated, b) after heating to 850 °C and holding under CO₂ for 10 s, and c) after CO₂ gasification to 80% conversion. The scale bar in b) applies to all three images.

3.3 Gasification inhibition

At conversions above 40-50% and temperatures above 800 °C, the rate of reaction decreased for CB-K₂CO₃-CaCO₃ compared to those for CB-K₂CO₃ (Fig. 1) and CB-K₂CO₃-BaCO₃ (Fig. 5). The effective activation energy for gasification of each mixture was calculated at different conversions (Fig. 7). The values for CB-K₂CO₃ varied from 265-280 kJ/mol over the range of conversion (10-90%) and were similar to those reported for K₂CO₃-catalyzed CO₂ gasification of ash-free coal (264 kJ/mol) [71] and ash-free wood char (279 kJ/mol) [39]. The addition of barium did not significantly change the activation energy (265-295 kJ/mol).

The activation energy in the presence of only calcium (CB-CaCO₃) was higher and varied from 300-350 kJ/mol. In the presence of both calcium and potassium (CB-K₂CO₃-CaCO₃), the activation energy decreased from 330 kJ/mol to 310 kJ/mol from 10 to 50% conversion and then to 150 kJ/mol at 90% conversion. The activation energy decreasing to 50% of its initial value suggests that the process became diffusion limited at higher conversions [72], which is consistent with the CaCO₃ coating the carbon particles and hindering diffusion of CO₂ to the CB. The

mobility of potassium may also have been affected. The variability in the activation energy was considerably higher in the presence of calcium (with or without potassium), possibly because of phase differences from 750 to 850 °C. The eutectic phase formation between K_2CO_3 and CaCO_3 at 822 °C has already been discussed; the Tammann softening temperature of CaCO_3 is 802 °C and may have led to variability when calcium was the sole catalyst. Calcium catalysts tend to deactivate during gasification by sintering [73]. Inhibition of the gasification was evident at 800 °C (Fig. 1), below the temperature at which the eutectic phase formed (Fig. 2).

Fig. 7. Activation energy versus conversion for CO_2 gasification CB with K_2CO_3 and/or CaCO_3 (CB- K_2CO_3 - BaCO_3 shortened to CB-K-Ba).

To further verify that the sintering of CaCO_3 was responsible for the inhibition, experiments were performed with a reduced amount of catalyst. At a catalyst to carbon ratio of 0.01, the gasification rates at 850 °C were similar with or without CaCO_3 up to 60% conversion (Fig. 8a). Previously, with a catalyst to carbon ratio of 0.1, the rate of gasification was enhanced with calcium (Fig. 1). Above 60% conversion, the rate with calcium was always lower (at 850 °C) but the rates differed by a factor of five or two for catalyst to carbon ratios of 0.1 and 0.01, respectively. The standard

deviation of the gasification rate for triplicate runs was approximately 0.014 min^{-1} , which was less than the difference between the two runs with catalyst to carbon ratio of 0.01 until 85% conversion (Fig. 8a). With lower amounts of catalyst, the potassium and calcium will be more dispersed and have less interaction, which was confirmed with SEM analysis (images not shown); hence, the minimal promotion at lower conversions. At higher conversions, the diffusion limitations will be lower with a lower Ca to carbon ratio but the CB particles eventually become coated (SEM images not shown).

Fig. 8. Impact of lower catalyst to carbon ratios: a) rate versus conversion for CO_2 gasification at 850°C of CB with K_2CO_3 or CaCO_3 and K_2CO_3 with a catalyst to carbon ratio of 0.01; b) activation energy of $\text{CB-K}_2\text{CO}_3\text{-CaCO}_3$ at different conversions for catalyst to carbon ratios of 0.01, 0.05 and 0.1.

The effective activation energy for $\text{CB-K}_2\text{CO}_3\text{-CaCO}_3$ mixtures with different catalyst to carbon ratios is shown in Fig. 8b. The trends are similar for ratios of 0.05 and 0.1, but the activation energy for the former ratio is lower, by 10-40 kJ/mol. In contrast, the activation energy was relatively constant for the mixtures with a catalyst to carbon ratio of 0.01, with the activation energy decreasing from 210 kJ/mol at 10% conversion to 180 kJ/mol at 90% conversion. Increased activation energy with increasing catalyst amounts has been reported in the literature [71, 74]. As

described in a previous publication from our group [71], the change in activation energy may be attributed to a change in the rate-determining step.

The optimal amount of catalyst for a commercial gasification process will depend on the operating conditions, as will the impact of eutectic formation. For example, molten catalysts have been shown to hinder the reaction rate in fluidized-bed gasifiers because they lead to defluidization [75]. Catalyst performance will also be affected by other constituents in the feed (e.g., silicon and aluminum [55, 76]). The study herein was designed to eliminate these other interactions in order to focus on the interaction between potassium and calcium. TGA was used to determine the presence of eutectic melting and its effect on the reaction rate. This behavior would still occur in large-scale industrial gasifiers, though the effect on rate would differ with gasifier design and feed composition. Thus, the interactions between calcium, potassium, and carbon observed using TGA can be applied to scaled-up gasifiers.

Although barium was an effective promoter of potassium, its natural scarcity in biosolids [53] and coal [77, 78] limits its industrial application. Use of intrinsic catalysts is desirable for gasification, to limit the costs associated with introducing a catalyst. Additionally, Ba^{2+} ions are toxic if ingested [79], and thus handling of barium compounds would necessitate additional safety precautions.

4. Conclusions

The gasification of CB was studied at temperatures between 750 °C and 850 °C in a thermogravimetric analyzer with various mixtures of K_2CO_3 and either CaCO_3 or BaCO_3 . Calcium promoted and inhibited the potassium-catalyzed gasification, depending on the conversion level and amount of catalyst. Formation of a eutectic mixture with a melting point of ~822 °C, enhanced

gasification above this temperature up to ~50% conversion for catalyst to carbon molar ratios of 0.05 or 0.1. At higher conversions, the sintering of CaCO_3 inhibited gasification by coating the CB and hindering the diffusion of CO_2 to the carbon. At a lower catalyst to carbon ratio of 0.01, the dispersion of potassium and calcium was sufficient to reduce their interaction and reduce the diffusion limitations. Similar to calcium, barium formed a eutectic phase with potassium, enhancing the gasification of CB. Unlike CaCO_3 , BaCO_3 does not sinter significantly at 850 °C and so promoted potassium to complete conversion.

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5. References

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