Comparison of surface area changes during sulfation of sodium bicarbonate in a simulated flue gas with and without NO

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Abstract

Sodium bicarbonate has been identified as one of the most efficient reagents for flue gas desulfurization. Sodium bicarbonate has been demonstrated both in bench scale and large scale applications by a number of researchers globally. Scattered reportings of plume discoloration during demonstrations of sodium bicarbonate injection have been attributed to the formation of the reddish-brown gas, NO\textsubscript{2}. To aid potential users from violating opacity regulations, impetus for further study of this extremely viable technology has been prompted. The purpose of this study was to compare the surface area changes of sodium bicarbonate during flue gas desulfurization (FGD) as it relates to the formation of NO\textsubscript{2}. The results of this study have indicated an anomalous behavior with respect to previously published data for non reactive gas environments. Notably it was shown that flue gas with NO lowered the surface area, most likely due to the formation of a low melting eutectic of sodium nitrate and sulfate. Nitrogen uptake was found to coincide with water evolution from decomposition. The results of this study more clearly define, on the microstructural level, the sulfur uptake mode. A unique laboratory differential fixed bed reactor was designed for this study. The setup included a quick quench zone to quench the reactions for data acquisition. BET surface area, IR elemental analysis, XRD crystalographic identification and SEM imaging were used to characterize microstructural mechanisms and to confirm reaction paths.

Introduction

Because of global population growth and industrial development, electric power generation by coal burning is on the rise, as is waste incineration. As a result, utilities and industries are motivated by national and international regulations to select and install flue gas desulfurization (FGD) systems for new and existing power plants and incinerators. The use of sodium bicarbonate for scrubbing has
been under development since the 1960's. It is of economic interest because of the very low capital investment needed to obtain very high sorbent utilisations for both new and retrofit systems. The technology has been successfully demonstrated in full scale by the Electric Power Research Institute (EPRI) in the U.S. and by Solvay in the E.C. SO$_2$ reductions of 70 - 90% were demonstrated (Bland$^1$). However, stack opacity observations during demonstration tests have seriously jeopardized commercial viability of this technology, despite the fact that overall exiting NO$_x$ levels are reduced by bicarbonate scrubbing. The reddish-brown plume coloration has been attributed to the formation of NO$_2$ by oxidation of flue gas NO by others. Over the past 15 years there have been many important findings from bench scale investigations linking the formation of NO$_2$ directly to the active removal of SO$_2$ (Knight$^3$, Bland$^1$). Nonetheless, the exact mechanism of formation of NO$_2$ is not well understood.

Thermal decomposition at an appropriate rate is necessary for the production of a high surface area carbonate for the concomitant reaction with SO$_2$ which is directly linked to the formation of NO$_2$. Surface area production due to decomposition has been well documented for non-reactive gas environments (Stern$^2$, Bland$^1$). Keener and Jiang$^3$ developed a decomposition model for surface area based on the work of Gregg. Decomposition versus time follow a peak/relaxation signature. During the peak period of decomposition, the sodium bicarbonate lattice is completely disrupted by the rapid evolution of water vapor and carbon dioxide. The peak is formed in the wake of vigorous decomposition. The initial dense, low surface area, solid sodium bicarbonate decomposes to a collection of very small, activated, metastable crystals or micelles of sodium carbonate. Relaxation is characterized by reordering of the micelles to a lower, more stable energy state. The lowest energy state for relaxation involves minimization of surface energy. During relaxation the micelles combine and grow by agglomeration, sintering and recrystalization, depending upon the melting point ratio, $T_m$, defined as the reactor temperature divided by the melting point of the micelles.

**Experimental Approach**

The experimental apparatus simulated sodium bicarbonate dry injection into a baghouse for flue gas desulfurization. The set-up consisted of injection of sodium bicarbonate into a gas stream which flowed into a differential fixed bed reactor. Reactions proceeded for specified time periods of 50, 200, 600, 3600 and 18,000 seconds. Experiments were conducted at 150°C and 250°C. Rapid quenching of the reactions was achieved by instantaneously transferring the powder to a quench zone. The resulting products were then analyzed for: specific surface area; carbon, hydrogen, nitrogen and sulfur content; microstructure and crystallographic identification. The flue gas was simulated by mixtures metered by precision needle valves. Three gas mixtures were investigated to study the effect of NO in flue gas: an inert gas (100% prepurified nitrogen); a simulated...
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flue gas mixture with NO (3000 ppm SO₂, 3.0% O₂, 3.5% CO₂, 2500 ppm NO, 46% He and balance N₂) and; a simulated flue gas mixture without NO (3000 ppm SO₂, 3% O₂, 14% CO₂ balance N₂). To simulate baghouse flow conditions, a gas velocity of 0.9 m/min was humidified to 3%. Injection was achieved via a ball-valve load lock. A 0.2 g sample of commercial-grade sodium bicarbonate supplied by Church and Dwight (3DF 30 micron average particle size) was loaded into the lock and injected down a heated, 48-cm long, 1.9-cm inner diameter, stainless steel tube into the isothermal fixed bed. The fixed bed was supported by a durable, woven stainless steel wire screen (325 x 2300 mesh), used to withstand the high-pressure transfer blast. One thermocouple was installed flush, upstream of the bed screen. Heat was supplied to the gas preheat zone, the injection pipe, and the isothermal zone. A high pressure gas pulse from below the fixed bed was used to transfer the powder from the isothermal zone through the transfer tube and into the quench zone. After the powder was transferred to the quench zone, a flow of chilled nitrogen gas was passed over the sample to quench the reaction. Specific surface area measurements were conducted using a Quantachrome Monosorb without outgassing. A LECO CHNS 932 Determinator, calibrated against standards, was used to measure 2.0 mg samples for carbon, hydrogen and sulfur. Microstructural analysis was conducted using a Cambridge 90B Scanning Electron Microscope (SEM) employing a 25 KV secondary electron beam. Photo images were made at 20,000x magnification. Crystallographic identification was conducted using a Rigaku D-2000 Powder X-Ray Diffractometer (XRD). The XRD samples were scanned using 40 KV, 40 MA from a 2-theta of 10 to 75 degrees, with a step size of 0.05 degree and a scan speed of 1 degree/min. The data peaks collected were matched using, Joint Committee on Powder Diffraction Standards, JCPDS, software.

Results

Surface area measurements are shown in Figure 1 at 150°C and 250°C for nitrogen gas and for flue gas with and without NO. Comparing the surface area curves in flue gas with and without NO to the surface area curves under nitrogen exhibits clearly that surface area is affected by the presence of flue gas reactions. Figure 1 shows that the general shape of the curves, follow the characteristic peak/relaxation curves that have been observed for calcium materials, (Keener and Jiang⁴). Table 1 lists the products formed after 18000 seconds as measured by XRD. The results of Table 1 corroborate well with the past findings of Howatson et al.⁵ for flue gas without NO identifying that a temperature dependant mixture of sodium sulfite and sodium sulfate (FormIII) is formed. The results also corroborate well with Bland⁶ showing that only sodium sulfate and sodium nitrate are formed regardless of temperature for flue gas with NO. Noteworthy, from Table 1 at 150°C for flue gas with NO, is the identification of sodium sulfate Form I found to coexist in solid solution with alpha phase sodium carbonate, isostructural with Na₂CO₃(SO₄)₂, sodium carbonate sulfate. Importantly this coexistence gives credibility to the concept of solid phase diffusion.
Table 1. Products formed after 18000 seconds of reaction

<table>
<thead>
<tr>
<th>Flue gas</th>
<th>150°C</th>
<th>ICPDS #</th>
<th>250°C</th>
<th>ICPDS #</th>
</tr>
</thead>
<tbody>
<tr>
<td>without NO</td>
<td>sodium sulfite</td>
<td>37-1488</td>
<td>sodium sulfate(III)</td>
<td>24-1132</td>
</tr>
<tr>
<td>with NO</td>
<td>sodium sulfate(III)</td>
<td>24-1132</td>
<td>sodium carbonate</td>
<td>19-1130</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>sodium $\text{Na}_2\text{CO}_3(\text{SO}_4)_2$</td>
<td>24-1134</td>
</tr>
</tbody>
</table>

For flue gas, the melting point ratio must use the melting point of the product layer formed immediately after peak decomposition rather then the bulk carbonate or the final product. Figure 2 compares the sulfur and nitrogen uptake at 150°C and 250°C for flue gas with and without NO. Note that sulfur and nitrogen are plotted together, sulfur on the left Y-axis and nitrogen on the right Y-axis. For the reactions in flue gas with NO Figure 2 shows that nitrogen and sulfur uptake occur during the peak decomposition interval for both 150°C and 250°C. A combination of sodium carbonate, sodium sulfate and sodium nitrate coexist on the micelles at the start of relaxation. A eutectic between sodium sulfate and sodium nitrate depresses the melting point of the combination to 301°C. Table 2 lists the calculated melting point ratios for the products postulated to form during peak decomposition for nitrogen gas, for flue gas without NO, and for flue gas without NO.

Table 2. Melting point ratio for product layer during decomposition

<table>
<thead>
<tr>
<th>Gas Type</th>
<th>Product</th>
<th>150°C</th>
<th>Tr</th>
<th>Product</th>
<th>250°C</th>
<th>Tr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen</td>
<td>$\text{Na}_2\text{CO}_3$</td>
<td>0.37</td>
<td></td>
<td>$\text{Na}_2\text{CO}_3$</td>
<td>0.46</td>
<td></td>
</tr>
<tr>
<td>no NO</td>
<td>$\text{Na}_2\text{SO}_3$</td>
<td>0.00</td>
<td></td>
<td>$\text{Na}_2\text{SO}_4/\text{NaNO}_3/\text{Na}_2\text{CO}_3$</td>
<td>0.48</td>
<td></td>
</tr>
<tr>
<td>with NO</td>
<td>$\text{Na}_2\text{SO}_4/\text{NaNO}_3/\text{Na}_2\text{CO}_3$</td>
<td>0.73</td>
<td></td>
<td>$\text{Na}_2\text{SO}_4/\text{NaNO}_3/\text{Na}_2\text{CO}_3$</td>
<td>0.91</td>
<td></td>
</tr>
</tbody>
</table>

Figure 1 shows that flue gas with NO notably lowered the overall surface area. Most dramatic is the drop in surface area at 250°C. The lower surface areas are explained by the formation of a tacky nitrate product described above. The melting point ratios in flue gas with NO are very high due to the nitrate. At 150°C strong contact welding is likely to occur and at 250°C extensive sintering is likely to occur. Figure 3 displays the high magnification (20,000X) SEM photomicrographs of sodium bicarbonate reacted for varying conditions. Figures 3a and 3b, show the products of decomposition under a nitrogen only environment at 150°C and 250°C. Both have the anticipated "popcorn-like" (nodular) porous microstructure (Bland1) but at 250°C the micelles have distinguishably coalesced and sintered into larger nodules. Figure 3c and 3d show the microstructures for reactions in flue gas without NO. The microstructures in flue gas without NO are very similar to those in nitrogen except that at 250°C the extent of sintering is much greater. Tracking the surface area for flue gas without NO in Figure 1 at 250°C also shows a more severe decline in surface area compared to the nitrogen gas environment. Figure 3e and 3f show the microstructures for flue gas with
NO. Despite the high melting point ratio listed in Table 2 at 150°C for NO the photo resembles the other 150°C microstructures, 3a and 3c. The extent of sintering at 150°C with NO is limited to the nitration period (3600 seconds from Figure 2) once nitration ceases the structure is stabilized and frozen by the subsequent sulfation reactions. Figure 3f shows the microstructure for flue gas with NO at 250°C. The microstructure structure is clearly very different. The structure is composed of large densely packed recrystalized grains. The surface area plot in Figure 1 shows that the surface area level dropped immediately after peak decomposition. Table 2 gives a melting point ratio of 0.91 nearly a liquid. Figure 2 shows that the nitration period is even shorter then at 150°C. It is postulated that instantaneous recrystalization is triggered by the almost liquidous nitrate mixture. Worthy of mention, decomposition dynamics were found to be inhibited by the presence of NO. After 600 seconds at 150°C only 50% conversion was recorded for flue gas with NO, while 85% and 91% conversion were recorded for flue gas without NO and nitrogen gas, respectively.

Figure 2 shows the sulfur and nitrogen uptake versus time at 150°C and 250°C. Very high sulfate conversion occurred for flue gas without NO, 77% and 98%, at 150°C and 250°C, respectively. However for flue gas with NO, sulfur uptake was markedly lower, 47% and 63 % at 150°C and 250°C, respectively. The sulfation rate was higher during the first 3600 seconds at all temperatures. Nitrogen uptake was significantly higher at 150°C compared to 250°C. Importantly, nitrogen uptake was greatest during decomposition when hydrogen was desorbing. (3600 seconds at 150°C and 600 seconds at 250°C) from the bicarbonate. After the nitration stopped and sulfation proceeded, a loss in the nitrate was measured at 250°C only.

Conclusions

Surface area changes of sodium bicarbonate particles were measured for a variety of reaction conditions; under nitrogen gas only, the surface area development follows that of similar type solids, and decreases with time at the higher temperature. However, in the presence of SO₂ and NO, anomalous behavior was observed. In the presence of NO, both peak and overall development were inhibited for both temperatures tested. This is most likely due to the presence of sodium nitrate compounds which form a low melting point eutectic.

REFERENCES

Figure 1 Specific Surface Area Comparison
Figure 2: Sulfur and Nitrogen Uptake Comparison

The sulfur axis is on the left and the nitrogen axis is on the right.
Figure 3: Microstructure Comparison.
Each photo is the surface of a single particle.