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SYNERGISTIC CAPTURE MECHANISMS FOR ALKALI AND SULPHUR SPECIES FROM COMBUSTION.

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SUMMARY

A number of sorbents with alumino-silicate base and sulfur capturing active sites have been developed for simultaneous removal of alkali metal compounds and sulfur dioxide. Current report will focus on bauxite sorbents, which includes experiments on sulfur dioxide absorption, alkali capturing and alkali / sulfur absorption simultaneously by bauxite-based sorbents. The alkali compound used here is sodium chloride. Experiments show an effective adsorption of sulfur or alkali separately, and the combined adsorption of alkali / sulfur. Atomic absorption analysis of reaction products shows that there is a much higher sodium existed in the combined reaction products than that of the single reaction of alkali absorption by bauxite. Further X-ray diffraction analysis shows that there is sodium sulfate in the final products of simultaneous reaction, which indicates the formation and then condensation of sodium sulfate in the reaction system.

EXPERIMENTAL APPROACH

Sample Preparation

The bauxite used here is called Paranam Bauxite from Alcoa Corporation which is commercially available. The bauxite first was sieved to retain the 60 to 80 mesh fraction, and then ready for the impregnation. The bauxite contains 11.0% of SiO_2 , 84.2% of Al_2O_3 and 4.8% of Fe_2O_3 ; the rest is considered trace material.

Calcium Acetate from Fisher Chemical was used for preparing calcium-containing solutions. Three solutions are prepared with a concentration of 5.1 mM, 10.2 mM and 15.3 mM.

There are two major impregnation processes. One is called incipient wetting technique (Sams, 1986). In this method, a carefully prepared amount of solid sample and solution is needed. The solution is just sufficient to thoroughly wet the solids and fill the pore volume. The method used here is called slurry. A moderate amount of solution is added to the solids to make them totally wet and to stir. After this, the slurry is dried in an oven at temperature of 200 °C for a couple of hours. The top part of the dried product is removed from the sample, which might be over saturated in calcium.

After the impregnating process was completed, the sample was then put in the oven to calcine under different temperature for two hours under the simulated flue gas condition. The bauxite remains the same chemical composition while the calcium acetate is oxidized and decomposed to calcium oxide, carbon dioxide and water. The reaction is as following:

The samples are then cut in 1 mm thick, 3 mm width and 4 mm length, and ready for use.

Reactor System Modification

The basic reactor system was given in Figure 1 in quarterly report No. 3. There are three major changes. One is adding two flow controllers for sulfur dioxide control and main nitrogen. The way it is designed right now, the controller for nitrogen can also be used to monitor the flow rate of air and carbon dioxide by applying a correction factor respectively. Those flow controllers are from MKS Instruments, Inc. They also have an RS-232 port to connect with computer for computer data acquisition and computer added control.

Another is the computer data acquisition system, which composes of a 386 personal IBM compatible computer and a LabPac hardware from the Scientific Solution, Inc. The main

software, calling for LabPac Library, was written in C language for our special use. This data acquisition system can also connect those flow controllers and control the flow rates where applied.

Finally, a pulsed fluorescent SO₂ analyzer of series 40, made by TECO Thermo Electron Corporation, is added to the system for the in- situ measurement of sulfur dioxide concentration. The instrument gives us a good and reliable result after carefully calibrated by standard SO₂ gas from the Matheson Gas Products, Inc.

A schematic diagram of the experimental system is given in Figure 1.

RESULTS AND DISCUSSION

The experiments consist of three main part, first part is the absorption of SO₂ by the impregnated sorbents and is aimed to explore the effect of solution concentration on the SO₂ capturing potency of the sorbent. Figure 2 gives the results of SO₂ adsorption by the sorbent at 800 °C at a SO₂ concentration of 270 ppm. The vertical axis shows the relative weight change of the sorbent monitored by the Cahn 2000 electronic balance, which gives milligrams of sulfur dioxide absorbed by per milligram sorbent. It can be seen that most of the reaction reaches the equilibrium after about 15 minutes reaction. The final conversions are different.

The sorbent with higher concentration of calcium solution has higher final conversion, which indicates that the higher of the solution, the richer the calcium is impregnated inside the sorbent, therefore the higher the calcium content in the sorbent. The rate of the SO₂ adsorption is given in Figure 3, the initial rate for sample number one is 0.0007 mg/mg.min, the rate for sample #3 is about 0.0008 mg/mg.min, which seems to show an increase of the initial rate with respect to the increase of the solution concentration. However, noticing that the rate of sample #2 with a concentration of solution 10.2 mM has a rate of about 0.001 mg/mg.min, a result of higher than both of sample #1 and #3. This evidence shows that the initial rate has a maximum value with respect to the solution concentration, or in other words, has an optimum point for the maximum initial rate. One possible explanation is that because the initial rate is directly proportional to the effective surface area of calcium particles, this surface area may reach a maximum value when increases the calcium solution concentration. When further increasing the concentration, the calcium content will increase because of the richer calcium solution, this may increase the calcium particle size but may not necessarily increase the surface area. On the other hand, because of the high concentration, some small calcium with high surface area will merge with each other and become a bigger particle, which causes possible decrease of surface area.

The SO₂ concentration effect on the adsorption is given in Figure 4. Comparing experimental results of concentration 82 ppm and 270 ppm, the former has a much longer conversion time of about 100 minutes and the later just have 15 minutes. And the initial rate

of the former is also much lower (Figure 5). But a same final conversion of 0.0064 mg/mg is observed. Those results show the diffusion effect on this first order reaction due to the concentration change. The same final conversion shows the limitation of SO₂ adsorption, which is only limited by the calcium content of the sorbent.

The distribution of calcium and sulfur inside the sample is obtained by the energy dispersion x-ray (EDX) analysis of computer-aided Scanning Electronic Microscope. The calcium element distribution shows a uniformly distributed pattern, which means the impregnation process has successfully sprouted out calcium active sites on the bauxite particles through out the sample. The sulfur distribution shows the same result with that of calcium, which indicates the relationship of sulfur absorbed by calcium.

Alkali adsorption by bauxite is given in Figure 6. Reaction temperature is 800 °C and the alkali source is 785 °C. Alkali vapor concentration is 230 ppm. Vertical axis represents the amount of sodium absorbed by unit sorbent. The reason to keep the source temperature lower than that of the reaction is to prevent condensation on the sorbent. The weight increases rapidly in the first fifteen hours, then slows down after that, and approaches a value of 0.13 mg/mg. The rate (see Figure 7) change vs. time almost linearly from the beginning of reaction to about 15 hours, and it tends to zero after thirty hours of experiment, which is a nindication of reaction completion.

The interaction of calcium on sodium removal is given in Figure 8. The same experimental conditions as those of Figure 6 are maintained for comparison. Sample #1 in the figure shows the adsorption of alkali vapor with bauxite sorbent, which is the same experiment given in Figure 6. The reaction almost stops after thirty hours Time, and reaches a final conversion of 0.13 mg/mg. For calcium impregnated sorbents, sample #2 and #3, the final conversions are the same with that of the calcium-free sample but the time is 80 hours and 120 hours respectively, which is much longer, in other words, a much longer time needed for the final conversion for calcium impregnated samples. The richer the calcium content, the longer the total conversion time, as concluded from this experiment results. This shows calcium sites will increase the diffusion resistance of alkali and decrease the mobility of alkali. The alkali adsorption rate is given in Figure 9, which gives a much higher initial rate of sample #1 of 0.013 mg/hr.mg, sample #2 0.008 mg/hr.mg and sample #3 of 0.004.

The mechanism of alkali adsorption by bauxite is not well understood yet. The sorbent tested here is bauxite which is mainly an aluminum-silica mixture. Which one, aluminum or silica, plays major contribution in alkali adsorption is of great interests and is investigated by EDX. The results are given in figure 11, in which aluminum, silicon, sodium and iron elements distribution in the sorbent are given in figure 11a through figure 11d ,respectively. Generally, aluminum rich area has less silica and vice versa. This confirms that bauxite is an aluminum-silica mixture structure not aluminum-silica compound like most of clay material, for example, kaolinite. Iron is just considered the trace material in the sample. Comparing

all the elemental distributions, a similar distribution of silica and alkali is found, which shows silica is probably the limitation for alkali adsorption by bauxite sorbent. Former research (Punjak, Shadman, Uberoi) shows the combined effect of aluminum-silica on alkali removal and the formation of alkali-aluminum-silicate. Because aluminum is greater stoichiometrically, silica content becomes limiting factor for alkali adsorption by bauxite.

Simultaneous adsorption of SO_2 and alkali is of the most interests in this research. Figure 10 shows a result of an experiment under the condition of 230 ppm concentration of alkali and 260 ppm of SO_2 at 800 °C of reaction temperature and 785 °C of alkali (NaCl) source temperature. The sample used here is bauxite with impregnating solution concentration of 5.1 mM. The result shows a final relative weight gain of about 80% of the initial sorbent, which is much higher compare to the single application of alkali adsorption of 13% (Figure 6). The reason is further explained in the following analysis of X-ray diffraction, X-energy dispersion SEM and Atomic adsorption. Because of the time scale, it is hard to see the initial behavior of the reaction from Figure 10. A closer look of the initial reaction rate is given in Figure 11. A significant weight change happened in the first 30 minutes which results in a relative weight gain of 1.5%. Comparing with Figure 2 of sample #1, a direct relationship is observed. In other words, the initial weight gain of simultaneous reaction is mainly contributed by the adsorption of SO_2 and minor by alkali adsorption. Although the initial rate of SO_2 /alkali adsorption is 0.0005 mg/mg.min, which is half the initial rate of SO_2 of 0.001 mg/mg.min, this may be due to the effect of alkali which will increase the initial diffusion

resistant of sulfur.

The first 15 hours of weight gain is about 18%, which is a higher than the combination of sulfur and alkali adsorption (14%). Further more, between 15 and 60 hours, the weight gain is almost linearly respect to time. This is a strong evidence of physical absorption or deposition. Therefore, it is suggesting three mechanisms contributing to the weight gain in this experiment: sulfur adsorption by calcium, alkali reaction with bauxite and condensation of sodium sulfate. The following solid sample analysis will further support this assumption.

Results suggest that sodium sulfate is condensed on the sorbent surface. If this is true, the condensation compound can be totally desorbed after the adsorption. The desorption experiment (Figure 12) gives a disappointing result which shows only a very small portion of the condensed material can be released through the desorption process under the experiment temperature and gas compositions. There are two possible explanations for this phenomenon. First the vapor pressure of sodium sulfate is very low; second, the sodium sulfate formation in the gas phase is over saturated, it forms a supersaturated sodium sulfate vapor. So that soon after the formation, it will condense on the porous bauxite sample. This is explained by the gas phase reaction of sodium chloride and sulfur dioxide. In the system, an excess SO_2 is presented, theoretically all the sodium chloride will convert to sodium sulfate which has a much lower vapor pressure than the sodium chloride at the same temperature, which results in the system temperature are far below the dew point at that concentration.

That is when the condensation happened.

Further study is needed to determine the details of the reaction and process mechanism.

CONCLUSIONS

Current work mainly focuses on the combined adsorption of sodium and sulfur by calcium impregnated bauxite. Following is a list of the main conclusions:

- 1) The calcium sites impregnated on the bauxite sorbent are effective for sulfur adsorption. They act as the regular lime sorbent for sulfur removal.
- 2) The bi-functional sorbents have the same potential for absorbing alkali vapor. The interaction of calcium on the adsorption of alkali is that the calcium sites will increase the diffusion resistant for the alkali vapor.
- 3) The combined adsorption of alkali/sulfur consists of three main steps. First, the adsorption of sulfur and possibly some reaction of alkali; second, combination of gas-phase reaction of alkali with sorbent and condensation of sodium sulfate; the last one is the possible condensation of sodium sulfate and molecular diffusion of alkali through the particles and

finding of active sites and then reaction. This sequence need to be further confirmed.

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Figure 1 A Schematic Diagram of Experimental Apparatus

Figure 2 Adsorption of SO₂ by Calcium-Impregnated Bauxite

Figure 3 Rate of sulfur dioxide adsorption

Concentration Effect on SO₂ Adsorption

Reaction Temperature: 800 °C
Solution Concentration: 5.1 mM

Figure 4 The Effect of SO₂ Concentration on Adsorption

Figure 5 Reaction Rate for SO₂ Adsorption

Figure 6 Adsorption of Alkali by Bauxite

Figure 7 Rate of Alkali Adsorption

Samples: Calcium Impregnated Bauxites

Solution Concentration:

#1 None; #2 5.1 mM; #3 15.3 mM

Gas Composition:

N_2 80%; CO_2 15%; O_2 3%; H_2O 2%

Figure 8 The Effect of Calcium Sites on Alkali Adsorption

Samples: Calcium Impregnated Bauxite

Solution Concentration:

1 None; #2 5.1 mM; #3 15.3 mM

Figure 9 Rate of Adsorption of alkali

Figure 10 Combined Adsorption of Alkali and Sulfur

Initial Adsorption of Alkali/Sulfur

Figure 11 Initial Adsorption of Alkali And Sulfur

Figure 12 Desorption of Simultaneous Reaction Sample

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