Use of TG-DSC-MS and Gas Analyzer Data to Investigate the Reaction of CO₂ and SO₂ with Ca(OH)₂ at Low Temperature

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To investigate the reaction of calcium hydroxide with CO₂ and SO₂ simultaneously, a gas containing both gases reacted with the calcium base at 58 °C and a relative humidity of 55 %. Different CO₂ and SO₂ concentrations were performed being the composition of the gas stream 12, 6 or 0 % CO₂; 5000, 2500, 1000 or 0 ppm SO₂, 9.5 % synthetic air and balanced N₂, with a flue gas rate of 1000 mL/minute. A continuous gas analyzer controlled the CO₂ and SO₂ concentrations in the effluent gas and the breakthrough curves of both gases were obtained. The gas analyzer data show that SO₂ and CO₂ compete to react with the base reacting simultaneously. By using thermogravimetry (TG), differential scanning calorimetry (DSC) and mass spectrometry (MS) techniques, calcium sulphite hemihydrate, CaSO₃.1/2H₂O, was identified as the unique desulfurization product detected. CaSO₄ was not identified although O₂ was present in the gas mixture. CaCO₃ was the main product of the reaction of calcium hydroxide and CO₂ being the complex CaO.CO₂ another possible product synthesized in low amounts. From analyzer data it was proved that a part of the CaCO₃ present in the sorbent or synthesized in the process reacts with the SO₂ and release CO₂. Results of this work show that the combination of continuous gas analyzer data and TG-DSC-MS techniques, not used before to study this reaction, is a good and easy way to clarify the process and the products of reaction.

1. Introduction

Coal combustion is one of the energy sources for electricity generation supplying the 12 % of Spanish electricity. The flue gas generated from the coal combustion power plant contains CO₂ (about 12%) and SO₂ at concentrations depending on the coal sulphur content, as well as NOx, H₂O, O₂ and N₂. Within the post combustion technologies developed to capture the SO₂ after the combustion, adsorption at low temperatures (up to 423 K) is considered one alternative with the added advantage that solids are easy to handle. In previous works different calcium hydroxide based sorbents have been prepared, analysed and used at low temperature, Renedo et al. (2006) and Renedo et al. (2012). To reduce cost in power production, Carter (2010) proposed the combined capture and storage of CO₂ and SO₂ or H₂S for conventional power plants. Kramer et al. (1997) stated the main reactions implied in the desulfurization process with Ca(OH)₂ when CO₂ was present and Li et al. (2000) working with Ca(OH)₂ injected in the flue gas, at temperatures about 500 °C, SO₂ concentrations of 3000 or 1500 ppm and CO₂ concentrations of 14 % found that the carbonation of the sorbent hinders the SO₂ capture even though slight alterations in CO₂ concentrations did not have significant effects on the SO₂ removal. Ho et al. (1996) proved that when O₂, CO₂ and SO₂ were present in the flue gas, the sulfation and carbonation reactions took place simultaneously and the carbonate formed, further reacted with SO₂ to form sulphite. Liu et al. (2010), working at the conditions similar to those in the bag filters of dry or semi dry Flue Gas Desulfurization (FGD) system, founded that when CO₂ and SO₂ were present, the final carbonate amount was lower than when only CO₂ is present because the CaCO₃ reacts with SO₂.
In a previous work, Fernández et al. (2010) found that CO\textsubscript{2} was mainly retained as CaCO\textsubscript{3} but also, in low amounts, as a CaO.CO\textsubscript{2} complex. These results were obtained in experiments of chemisorption of CO\textsubscript{2} at 50 °C that were performed with a dry flue gas (10% CO\textsubscript{2} in He), commercial Ca(OH)\textsubscript{2} and with calcium hydroxide supported on mesoporous materials.

In the present work, the process of simultaneous SO\textsubscript{2} and CO\textsubscript{2} capture, at their usual concentrations in a coal combustion flue gas by calcium hydroxide at low temperature is studied. The objectives were to know the reaction process and the products synthesized based on the CO\textsubscript{2} and SO\textsubscript{2} continuous analyzer data and on the results found analyzing the reacted sorbent by thermogravimetry (TG), differential scanning calorimetry (DSC) and mass spectrometry (MS) techniques.

2. Experimental procedure

A commercial Ca(OH)\textsubscript{2}, supplied by Calcino S.A., was used as sorbent and the desulfurization reaction was performed in the laboratory experimental set-up, shown in Figure 1. The gas stream without SO\textsubscript{2} passed through the humidification system. After humidification, the gas mixture with SO\textsubscript{2} flowed through the reactor that contained one gram of the sorbent dispersed in 30 g of inert silica sand at 55 % of relative humidity and at temperature of 58 °C. The composition of the gas stream was: 12, 6 or 0 % CO\textsubscript{2}; 9.5 % synthetic air; 5000, 2500, 1000 or 0 ppm SO\textsubscript{2} and balanced N\textsubscript{2} being 1000 mL/minute the flue gas rate.

![Experimental set up of the reaction process](image)

Figure 1: Experimental set up of the reaction process

The concentration of SO\textsubscript{2} and CO\textsubscript{2} after the reaction was continuously monitored in an Emerson MLT-1 NGA 2000 gas analyzer and data were compiled with a personal computer equipped with a NGA win control software. The breakthrough curves of both gases were plotted with the analyzer data. When the reaction time was over, 1 hour approximately, (controlled by the breakthrough curves), the reacted sorbent was sieved to separate it from the sand. Some of the reacted sorbents were submitted to TG, DSC and MS analysis. A Setaram thermal analyzer model SETSYS-1700 was used for the TG and DSC curves determination. This TG instrument was coupled to a Balzers Thermostar/Omnistro mass spectrometer (Pfeiffer vacuum) for evolved gas analysis. The carrier gas used was N\textsubscript{2} at a flue rate of 100 mL/min and the temperature was increased from room temperature to 1350 °C at 10 °C/min. The number of m/z signals selected corresponds to H\textsubscript{2}O (18), SO\textsubscript{2} (64), SO\textsubscript{3} (80) and CO\textsubscript{2} (44).

3. Results and Discussion

3.1 Reaction process

Before starting the desulfurization reaction, there is an initial stabilization period in which the gas mixture does not pass through the reactor. After this period, the gas leaving the reactor passes through two ice traps to condense the water content before getting the analyser. Figure 2 shows the breakthrough curves of CO\textsubscript{2} and SO\textsubscript{2} for a run with about 12 % of CO\textsubscript{2} and 5000 ppm of SO\textsubscript{2}. The first horizontal zone corresponds to the gases concentration stabilization.
Figure 2: Breakthrough curves of SO$_2$ and CO$_2$ for one experiment with a flue gas containing 12 % of CO$_2$ and 5000 ppm of SO$_2$

Figure 2 shows that both gases react simultaneously with the calcium hydroxide according to Ho et al. (1996). Furthermore, the CO$_2$ breakthrough curve shows at about 600 s of reaction, a gas concentration higher than the initial one due to the reaction of SO$_2$ with CaCO$_3$ that release CO$_2$.

From analyzer data, curves of mol SO$_2$ or mol of CO$_2$ captured versus time were drawn. Figures 3 and 4 show both curves.

Figure 3: Mol of SO$_2$ captured for a CO$_2$ concentration of 12 % and a SO$_2$ concentrations of 5,000, 2,500 or 1,000 ppm and 0 % of CO$_2$ with 5000 ppm of SO$_2$.
Comparing Figures 3 and 4, different shapes mainly at the beginning of the process are found. These different shapes are principally due to the great differences in SO$_2$ and CO$_2$ concentration in the gas mixture and in consequence to a great difference in their reaction rates. Figure 4 shows a first step in which the reaction of Ca(OH)$_2$ with CO$_2$ is very fast, in a process chemically controlled; this step is followed by a period diffusionally controlled with a slow CO$_2$ capture or even with no appreciable capture. In all runs performed with both gases, except in experiments with 12 % CO$_2$ and 1,000 ppm SO$_2$, there is a time period, at about 600 seconds, with values of CO$_2$ concentrations higher than the initial one. These results only can be explained considering a net CO$_2$ production. The CaCO$_3$ present in the sorbent or produced in the reaction of Ca(OH)$_2$ and CO$_2$, reacts with SO$_2$, a stronger acid than CO$_2$, and release CO$_2$. Although this reaction occurs all the time, only when the amount of CO$_2$ captured is lower than the amount of this gas released, a net CO$_2$ emission is detected. These results obtained from analyzer data are confirmed by MS analysis. Figures 3 and 4 also show the competence between both acid gases to react with the base as the highest SO$_2$ or CO$_2$ captures are obtained when only one gas is present in the process: experiments with (5000 ppm SO$_2$ / 0 % CO$_2$ and 12 % CO$_2$ and 0 ppm of SO$_2$).

3.2 Products of the Reaction

TG, DSC and MS results of the sorbent allow us to complete the study of the reaction process and to know the products of the reaction. Figure 5 shows the TG curve corresponding to the Ca(OH)$_2$ after the reaction with CO$_2$ (12 %) and SO$_2$ (5,000 ppm) as well as DSC and MS curves for this run. (The rest of the TG curves are omitted).

TG curve shows a first mass loss (near 125 °C) due to the loss of humidity, followed by other two dehydration processes: the water of the product CaSO$_3$.1/2 H$_2$O (at about 360 °C) and the Ca(OH)$_2$ dehydration at the temperature range of 370-465 °C. These water losses were confirmed by three endothermic peaks in the DSC curve and three signals of water emission (m/z = 18) in the MS curve.

At the temperature range of 554-850 °C, TG curve shows a mass loss due to the CaCO$_3$ calcination and DSC curve presents two endothermic peaks and MS curve shows two overlapped signals of CO$_2$ emission (m/z = 44) that can be attributed to the calcination of the CaCO$_3$ present in the sorbent and of that synthesized in the process.
A small peak of CO\(_2\), within 425-525 °C is attributed to the decomposition of the CaO.CO\(_2\) complex identified in a previous work by Fernández et al. (2010). The low intensity of this peak is due to the CO\(_2\) scale with an intense CO\(_2\) emission peak in the range of the calcination temperature. The synthesis of this complex is also suggested considering the TG mass losses of the sorbent after the reaction with CO\(_2\) alone (experiment 0 ppm SO\(_2\) /12 % CO\(_2\)). This TG is not shown. In this run, the moles of Ca(OH)\(_2\) reacted should be equal to the moles of CaCO\(_3\) formed, but that amount, calculated from the TG mass loss, was higher than the CaCO\(_3\) formed suggesting that another product of the reaction between CO\(_2\) and Ca(OH)\(_2\) must be synthesized.

Three peaks of molecular weight 64, at about 725, 1,000 and 1,250 °C were identified by MS. Last one is probably due to the decomposition of a sulphur compound present in the commercial calcium hydroxide as this peak also appears in the TG of this calcium hydroxide. Commercial calcium hydroxide contains as impurity compounds of sulphur at 0.067 % and 0.168 % of SO\(_3\). The peak at about 1000 °C corresponds to the CaSO\(_3\) synthesized in the reaction and the first one detected within 725 and 875 °C, not present in the initial calcium hydroxide, was also found after the reaction with a gas without SO\(_2\) and hence cannot corresponds to SO\(_2\).

From mass loss values at about 360 °C and in the range 875-1,025 °C in can be deduced that CaSO\(_3\).1/2 H\(_2\)O is the desulfurization product synthesized. The presence of SO\(_3\) with a molecular weight of 80, corresponding to the CaSO\(_3\) decomposition, was also investigated but it was not detected showing that this product has not been synthesized though O\(_2\) is present in the flue gas.

As a summary of TG, DSC and MS results it can state that CaSO\(_4\) is not a product of desulfurization reaction at low temperature, being CaSO\(_3\).1/2 H\(_2\)O the unique desulfurization product. CaCO\(_3\) is the main product of CO\(_2\) capture and CaO.CO\(_2\) another one. DSC and MS data allows distinguishing the calcination of the CaCO\(_3\) formed from the CO\(_2\) captured than that present in the initial sorbent.

4. Conclusions

The study of the reaction of CO\(_2\) and SO\(_2\) with commercial calcium hydroxide at low temperature in a continuous gas analyzer proves and quantifies the simultaneous reaction of the sorbent with both gases and the CO\(_2\) release in the reaction of CaCO\(_3\) with SO\(_2\).

According to TG-DSC-MS results, the unique reaction product of calcium hydroxide and SO\(_2\) at this low temperature, despite the presence of O\(_2\), is CaSO\(_3\).1/2 H\(_2\)O. The main product of the reaction of CO\(_2\) and
Ca(OH)₂ is CaCO₃. The detection by MS of little amounts of CO₂ released within 425-525 °C and the difference between the Ca(OH)₂ reacted and the CaCO₃ formed when SO₂ is not present, suggest the possible formation of a CaO.CO₂ complex, postulated in a previous work.

Data of the gas analyzer and TG-DSC-MS techniques allows discussing the evolution of the CaCO₃ present in the sorbent, synthesized in the reaction with CO₂ or disappeared by reaction with SO₂. According to the results of the present study, in future works, the use of calcium hydroxide or of sorbents based on this compound at higher temperature will be investigated.

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