

On the CO₂ and H₂O chemisorption on hydrotalcite-based adsorbents for sorption-enhanced water-gas-shift processes

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Abstract

Thermogravimetric analysis (TGA) was used to study the adsorption phenomena of CO₂ and H₂O on a hydrotalcite-based adsorbent to be used for sorption-enhanced Water-Gas-Shift (SEWGS). The adsorption of CO₂ and H₂O and the interaction between the two can be described when considering the presence of at least three different sites (2 for CO₂ and 1 for H₂O) participating in the adsorption phenomena at elevated temperatures. The experiments confirm that the regeneration conditions are crucial for activating more sites for CO₂ adsorption and are therefore the limiting factor for the cyclic working capacity of the adsorbent.

Keywords

Cyclic working capacity, CO₂ sorption kinetics, Hydrotalcite

Introduction

The sorption-enhanced Water-Gas-Shift process (SEWGS) is a promising novel technology for hydrogen production with integrated CO₂ capture. SEWGS involves the capture of CO₂ in a sorbent material during the water-gas shift reaction. A pure CO₂ stream, which is obtained during sorbent regeneration with steam and further steam condensation, can be directly used for carbon storage (Boon et al. 2014). Hydrotalcite-based adsorbents have been investigated as possible candidates for the adsorption of CO₂ at elevated temperatures and pressures due to their high stability, relatively fast adsorption/desorption kinetics and high CO₂ capacity.

However, the interactions between small gas molecules such as H₂O, CO₂ and H₂S and the adsorbent are still not fully understood. It has been reported that steam enhances the CO₂ sorption capacity of hydrotalcite-based adsorbents (Maroño et al. 2014), but detailed understanding combined with a quantitative description of the interactions between H₂O and CO₂ in a mixed sorption system, is still lacking in the literature.

In a previous work the cyclic working capacity of a hydrotalcite-based adsorbent has been defined and measured for pure components H₂O and CO₂. It was found that the desorption step mainly determines the cyclic working capacity because of slow desorption kinetics and that the mechanism for CO₂ and H₂O adsorption is different (Coenen et al. 2015). In this study, the influence of H₂O on the cyclic working capacity of CO₂ and the possible interactions of both gaseous species is investigated in more detail using thermogravimetric analysis. On the basis of the experimental data a model is

developed to describe the measured adsorption working capacities.

Material & Methodology

Thermogravimetric Analysis (TGA) was used to study the adsorption and desorption kinetics of a potassium promoted hydrotalcite-based adsorbent with a molar Mg/Al ratio of 0.54. The experiments were divided in 8 different cycles containing different adsorption and regeneration steps. Each cycle was repeated 5 times. The average weight change between every step of the last three measurements of each cycle were used to determine the cyclic working capacity of the adsorbent. The measured weight change was corrected with a blank experiment to correct for density changes between the feed gases. Table 1 shows the carefully devised cycle procedure description for the experiments.

Table 1. Cycle procedure description

| NO | Experimental cycle description | Steps in cycle | cycle time (min) |
|----|--|----------------|------------------|
| 1 | H ₂ O/N ₂ ⇌ N ₂ | 2 | 60 |
| 2 | CO ₂ ⇌ N ₂ | 2 | 60 |
| 3 | CO ₂ ⇌ N ₂ ⇌ N ₂ /H ₂ O ⇌ N ₂ | 4 | 120 |
| 4 | CO ₂ /H ₂ O ⇌ CO ₂ ⇌ N ₂ ⇌ N ₂ /H ₂ O ⇌ N ₂ | 5 | 150 |
| 5 | CO ₂ ⇌ CO ₂ /H ₂ O ⇌ N ₂ ⇌ N ₂ /H ₂ O ⇌ N ₂ | 5 | 150 |
| 6 | CO ₂ /H ₂ O ⇌ N ₂ ⇌ N ₂ /H ₂ O ⇌ N ₂ | 4 | 120 |
| 7 | CO ₂ /H ₂ O ⇌ N ₂ /H ₂ O | 2 | 60 |
| 8 | CO ₂ /H ₂ O ⇌ N ₂ /H ₂ O ⇌ N ₂ | 3 | 90 |

The base case experiment was designed at 400 °C with 30 min for each step in one cycle. The used molar fraction was 0.66 for CO₂ and 0.34 for H₂O respectively. The cyclic working capacity of the adsorbent was measured at

temperatures between 300 and 500 °C and between atmospheric pressure and 8 bar (g). Subsequently, different partial pressures of the adsorbates CO₂ and H₂O were used. Table 2 shows the different temperatures and molar fractions used.

Table 2. Different Settings used in Experiments

| | Base case | Variations in Settings | | |
|-------------------------------|-----------|------------------------|-----|-----|
| Temperature (°C) | 400 | 300 | 400 | 500 |
| CO ₂ fraction (-) | 0.66 | 0.2 | 0.4 | 0.6 |
| H ₂ O fraction (-) | 0.34 | 0.1 | 0.2 | 0.3 |
| Total Pressure (bar) | 1 | 2 | 4 | 6 |

Experimental Results

Figure 1 shows the results for the base case experiment for the eight different cycles and the normalized weight change of the material during the different adsorption/regeneration steps.

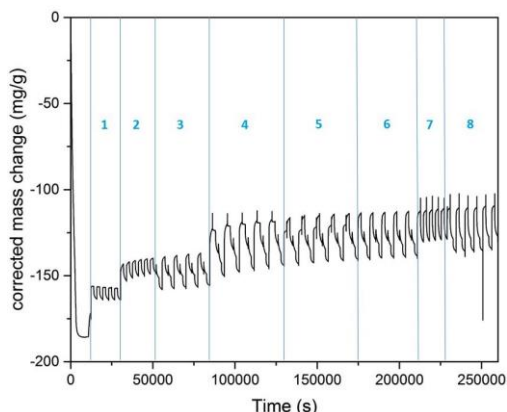


Figure 1. TGA base case experiment at 400 °C

From the interpretation of the experimental results, the weight changes during the different cycles in the different experiments could be assigned to different sites according to Table 3 (for the base case experiment).

Table 3. Cyclic working capacities for CO₂ and H₂O

| | | | |
|---|----|------|--|
| site for H ₂ O | 8 | mg/g | |
| site 1 for CO ₂ | 12 | mg/g | dry regeneration (N ₂) |
| site 2 for CO ₂ | 11 | mg/g | wet regeneration (N ₂ + H ₂ O) |
| adsorption of CO ₂ | 23 | mg/g | |
| co-adsorption of CO ₂ & H ₂ O | 31 | mg/g | |

After modeling the experimental results, it was concluded that the material has at least two different sites available for CO₂ and one independent site for H₂O. Under dry (N₂ only) regeneration conditions only one CO₂ site can be regenerated. If H₂O is used during the regeneration step, both sites for CO₂ can be regenerated explaining the higher cyclic adsorption capacities for CO₂ (Table 3). Experiments with co-adsorption of CO₂ and H₂O showed a weight increase between 30 and 32 mg/g, which corresponds nicely to the expected weight change considering the three sites and independent adsorption of H₂O. Figure 2 shows the proposed mechanism for CO₂ and H₂O adsorption with the different sites involved at

adsorption and regeneration conditions for a SEWGS process in a packed-bed reactor system. Experiments at higher temperatures show similar results to the results reported for the base case which confirm that the proposed model is valid at different experimental conditions.

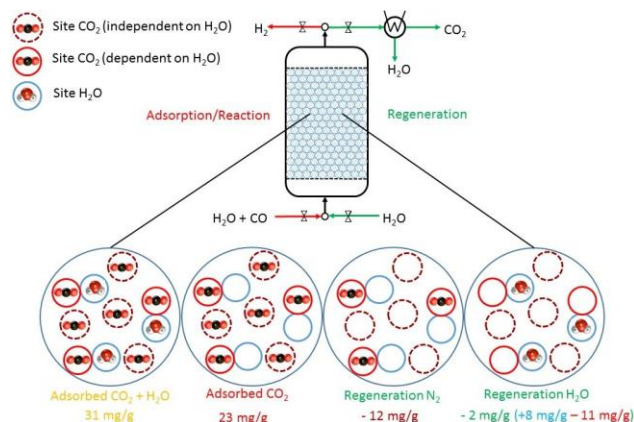


Figure 2. Three different sites involved in CO₂ and H₂O adsorption at different conditions

Conclusions

Using smart designed TGA cycles three different sites could be identified which are participating in the adsorption phenomena of CO₂ and H₂O. It was found that H₂O increases the cyclic working capacity of CO₂ by additional desorption of CO₂ during the regeneration step. Therefore, the regeneration conditions during sorption-enhanced water-gas-shift are very important, not only because the relatively slow desorption kinetics determine the cyclic working capacity to a large extent, but also because the activation of the different sites depends on the gas composition during this step. A model has been developed on the basis of the proposed mechanism that can describe the cyclic adsorption phenomena on this adsorbent quite well.

Acknowledgments

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