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Citation for published version (APA):

Coenen, K., Gallucci, F., Hensen, E., & van Sint Annaland, M. (2018). Adsorption behavior and kinetics of H₂S on a potassium-promoted hydrotalcite. *International Journal of Hydrogen Energy*, 43(45), 20758-20771. ²
<https://doi.org/10.1016/j.ijhydene.2018.09.146>

Document license:
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DOI:
[10.1016/j.ijhydene.2018.09.146](https://doi.org/10.1016/j.ijhydene.2018.09.146)

Document status and date:
Published: 08/11/2018

Document Version:
Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

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Adsorption behavior and kinetics of H₂S on a potassium-promoted hydrotalcite

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ARTICLE INFO

Article history:

Received 10 July 2018

Received in revised form

16 September 2018

Accepted 21 September 2018

Available online 16 October 2018

Keywords:

SEWGS

H₂S adsorption

Interaction of H₂S H₂O and CO₂

Cyclic working capacity

ABSTRACT

Adsorption of H₂S and the influence of steam on its adsorption capacity and kinetics were studied on a commercial potassium-promoted hydrotalcite. The sorbent shows a very high cyclic working capacity for H₂S compared to CO₂ and H₂O, even at lower partial pressures and at different operating temperatures ranging between 300 and 500 °C. The operating temperature does not significantly influence the cyclic working capacity for half-cycle times of 30 min. The adsorption mechanism, however, changes at higher temperatures. At lower temperatures (300 °C) a fast adsorption with a fast approach to steady state was observed. At higher operating temperatures, H₂S reacts with the hydrotalcite structure, forming strongly bonded sulfuric species on the sorbent. When using dry regeneration conditions, the first cycles in cyclic operation at higher temperatures show a significantly higher adsorption of H₂S (especially the first cycle), which cannot be desorbed during regeneration with N₂. After the first fast initial adsorption rate a continuous slow adsorption of H₂S occurs, probably caused by a surface reaction between H₂S and the hydrotalcite structure. This reaction is, however, reversible if steam is used.

The adsorption mechanism for H₂S and H₂O was determined using multiple cyclic experiments comparable to previous studies performed for CO₂ and H₂O adsorption. It is evident that the adsorption mechanism developed for CO₂ on the same sorbents is also valid for H₂S, indicating that the developed mechanism is consistent for sour gas adsorption on this type of sorbents. The cyclic working capacity can be significantly increased if steam is used during the regeneration step of the sorbent. The mechanistic model developed for the adsorption of CO₂ and H₂O was successfully validated with more than 160 different TGA experiments. An operating temperature of 400 °C seems to be optimal to achieve a high cyclic working capacity for H₂S, because at higher temperatures the regeneration of the formed sulfuric species seems to be hindered resulting in a significant decrease in the cyclic working capacity.

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<https://doi.org/10.1016/j.ijhydene.2018.09.146>

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Nomenclature

CCS	carbon capture and storage
CWC	cyclic working capacity
HTC	hydrotalcite
FTIR	Fourier transform infrared spectroscopy
KMG30	potassium promoted hydrotalcite with 30 w% MgO compared to Al ₂ O ₃ (sorbent material)
PBR	packed bed reactor
P _{CO2}	partial pressure of CO ₂ [bar]
P _{H2O}	partial pressure of H ₂ O [bar]
P _{H2S}	partial pressure of H ₂ S [bar]
SEWGS	sorption enhanced water-gas shift reaction
TGA	thermo-gravimetric analysis

Introduction

Hydrogen is a large-scale chemical product and used for different chemical processes such as ammonia synthesis, methanol production and petroleum refining. Usually hydrogen is produced based on fossil fuels such as natural gas, oil or coal. The total annual carbon emissions for hydrogen production is 255 Mt (H₂ production from natural gas) and 518 Mt from coal plants. Carbon capture and storage (CCS) has the potential to reduce these emissions to 42 Mt and 83 Mt, respectively [1]. The sorption enhanced water-gas shift (SEWGS) process is a promising technology for in-situ CO₂ capture and hydrogen production [2]. SEWGS is a kind of pressure swing adsorption (PSA) process, where CO₂ is reversibly adsorbing on solid materials during the water gas shift reaction [3]. It enables direct conversion of syngas into separate streams of H₂ and CO₂ [4]. It has been demonstrated that hydrotalcite-based adsorbents have a high carbon capture efficiency, sufficiently fast adsorption and desorption kinetics and have been proven mechanically stable over thousands of cycles making them ideal candidates for their application in SEWGS processes [5–7]. Hydrotalcites belong to the group of anionic clays, where the most common one is the double magnesium-aluminum hydroxide Mg₆Al₂(OH)₁₆CO₃²⁻ × 4H₂O. It has been reported frequently that K₂CO₃ promotion can increase the sorption capacity for CO₂ due to an increase of its surface basicity [8–10].

The adsorption kinetics and capacity and the interaction of CO₂ and H₂O were investigated for a commercial potassium-promoted hydrotalcite in previous works [11–13]. It was found that slow desorption kinetics mainly determine the cyclic working capacity of CO₂ and H₂O. A mechanism has been proposed including at least three different sorption sites for CO₂ and H₂O, which has been proven to be valid for hydrotalcite-based adsorbents with different Mg/Al ratios and for potassium-promoted alumina [14,15]. It has been found that usually one adsorption site for both H₂O and CO₂ are present, which can be regenerated with N₂. Additionally, one adsorption site is present which can only be exchanged by another interacting sorbate species. If both sorbate species are present in the gas stream, depending on their partial pressure, this last site will be partly occupied by each sorbate.

Syngas from coal in an integrated gasification combined cycle (IGCC) power plant can contain H₂S from few ppm to a few per cent [16]. Therefore, the interaction between H₂S and the adsorbent, as well as the interaction of H₂S on the adsorption capacity of CO₂ and the possible appearance of H₂S in the hydrogen stream needs to be investigated and quantified in detail. A mechanism for the interaction between CO₂ and H₂S has been presented in the past involving two different adsorption sites for H₂S on a commercial potassium-promoted hydrotalcite with a Mg/Al ratio of 2.9 [17,18]. In general, mixed metal oxides have shown high H₂S sorption capacities for H₂S removal at low [19–22] and also elevated temperatures [23]. The interaction of H₂S with a commercial potassium-promoted hydrotalcite and the influence on the developed mechanism for CO₂ and H₂O adsorption is investigated in detail in this work. Thermogravimetric analysis (TGA) and packed bed reactor (PBR) breakthrough experiments were used to study and quantify the interaction of binary sorbate mixtures such as H₂S and H₂O and H₂S and CO₂ and ternary mixtures with CO₂, H₂O and H₂S.

Materials and methods

A potassium-promoted hydrotalcite-based adsorbent with a Mg/Al ratio of 0.54 and a potassium loading of approximately 20 wt%, produced by Sasol (Germany), was used in the experiments and will be further denoted as KMG30. The original pellets (4 mm × 4 mm) were milled to a powder for TGA experiments with a mean average diameter of about 40 μm, or crushed for packed bed reactor experiments with a sieve fraction between 1.8 and 3.15 mm. Sample weights for the TGA experiments were around 100 mg, while the packed bed reactor with an inner diameter of 27 mm was filled with 54.9 g of KMG30 resulting in a packed bed height of approx. 17 cm. The TGA and PBR experiments and setups are described in detail in an earlier publication [15], where the packed bed reactor was installed in this case in the same setup related to the additional safety measures for H₂S experiments. Gas analysis for the breakthrough experiments was performed with two different gas analyzers. For H₂S, H₂, CO and CO₂ a SICK GMS800 analyzer was used with different modules, where only a dry gas stream could be measured, hence requiring prior steam condensation. H₂O and CO₂ was independently measured by an Agilent Technologies Cary 630 FTIR with CaF₂ windows used together with a RED-SHIFT gas sampling system installed before the condenser.

An overview of the different experiments performed to study the adsorption behavior and kinetics of H₂S on KMG30 is provided in Table 1. H₂S adsorption was studied with experiments 1–3 (Table 1), where the sorbent was regenerated with N₂ after H₂S adsorption and a half-cycle time of 60 min was used for each adsorption and regeneration step. The adsorption interactions between H₂O on H₂S was studied with TGA experiments 4–7 and 9–10 in the packed bed reactor. CO₂ and H₂S interaction was studied with experiment 8 with TGA and experiments 11–13 in the packed bed. Ternary mixtures of CO₂, H₂S and H₂O were studied in the packed bed only (experiments 14–15), since a weight change measured with TGA cannot be easily assigned to individual sorbate species being

Table 1 – Overview of different experiments performed to study the adsorption behavior and kinetics of H₂S on KMG30.

NO	Method	Temperature °C	PCO ₂ bar	PH ₂ O bar	PH ₂ S bar	PH ₂ bar	Experiments	EXP
1	TGA	300	0	0	0.05	0	10	2
2	TGA	400	0	0	0.05	0	10	2
3	TGA	500	0	0	0.05	0	10	2
4	TGA	400	0	0.34	0.03	0.025/0	40	1–8
5	TGA	400	0	0.34	0.02	0	40	1–8
6	TGA	400	0	0.2	0.02	0	40	1–8
7	TGA	400	0	0.1	0.02	0	40	1–8
8	TGA	400	0.05	0	0.03	0.025	40	9–16
9	PBR	400	0	0.1	0.03	0	16	1–8
10	PBR	300	0	0.1	0.03	0	16	1–8
11	PBR	300	0.05	0	0.03	0.025	16	9–16
12	PBR	400	0.05	0	0.03	0.025	16	9–16
13	PBR	500	0.05	0	0.03	0.025	16	6–16
14	PBR	400	0.05	0.1	0.03	0.025	9	1–8
15	PBR	400	0.05–0.15	0.1–0.2	0.03	0.025	10	1–8

adsorbed or desorbed in a ternary system. Each experiment contains a certain number of adsorption/regeneration steps in order to investigate the sorbate–sorbent interaction. These steps are specified in Table 2. The absence of external mass transfer limitations was proven by comparing the adsorption rate of H₂S at different gas flow rates in the TGA. Note that the experiments in the packed bed reactor were always carried out with 0.025 bar of H₂ in the feed gas stream to prevent irreversible adsorption of H₂S on the sorbent material, which has been proven with TGA experiments and will be described in more detail in the subsequent sections.

Results and discussion

Adsorption and desorption of H₂S at different operating temperatures

Adsorption of H₂S and regeneration with N₂ was studied at three different operating temperatures according to

Table 2 – Description of different steps in one cycle of a certain experiment according to Table 1.

EXP	cycle description	Steps in cycle	cycle time (min)
1	H ₂ O/N ₂ ⇌ N ₂	2	60
2	H ₂ S ⇌ N ₂	2	60
3	H ₂ S ⇌ N ₂ ⇌ N ₂ /H ₂ O ⇌ N ₂	4	120
4	H ₂ S/H ₂ O ⇌ H ₂ S ⇌ N ₂ ⇌ N ₂ /H ₂ O ⇌ N ₂	5	150
5	H ₂ S ⇌ H ₂ S/H ₂ O ⇌ N ₂ ⇌ N ₂ /H ₂ O ⇌ N ₂	5	150
6	H ₂ S/H ₂ O ⇌ N ₂ ⇌ N ₂ /H ₂ O ⇌ N ₂	4	120
7	H ₂ S/H ₂ O ⇌ N ₂ /H ₂ O	2	60
8	H ₂ S/H ₂ O ⇌ N ₂ /H ₂ O ⇌ N ₂	3	90
9	CO ₂ /N ₂ ⇌ N ₂	2	60
10	H ₂ S ⇌ N ₂	2	60
11	H ₂ S ⇌ N ₂ ⇌ N ₂ /CO ₂ ⇌ N ₂	4	120
12	H ₂ S/CO ₂ ⇌ H ₂ S ⇌ N ₂ ⇌ N ₂ /CO ₂ ⇌ N ₂	5	150
13	H ₂ S ⇌ H ₂ S/CO ₂ ⇌ N ₂ ⇌ N ₂ /CO ₂ ⇌ N ₂	5	150
14	H ₂ S/CO ₂ ⇌ N ₂ ⇌ N ₂ /CO ₂ ⇌ N ₂	4	120
15	H ₂ S/CO ₂ ⇌ N ₂ /CO ₂	2	60
16	H ₂ S/CO ₂ ⇌ N ₂ /CO ₂ ⇌ N ₂	3	90

experiments 1–3 (Table 1). The weight change during adsorption and desorption after pretreatment of the sorbent (as described previously) is shown in Fig. 1a, while the amount of adsorbed, desorbed and irreversibly adsorbed H₂S at 300, 400 and 500 °C are plotted in Fig. 1b–d respectively. The operating temperature has a major influence on the adsorption and regeneration behavior of H₂S on KGM30. In general, during the first cycle a large amount of H₂S is adsorbed compared to the other cycles. Similar results have been recently published for CO₂ for the same material [11].

While at 300 °C a pseudo steady state (i.e. same amount of H₂S desorbed as adsorbed in the previous step) is achieved quite quickly, whereas at 400 °C a constant mass increase over the cycles is observed. The amount of irreversibly adsorbed H₂S during the first cycle (about 0.5 mmol/g) is very similar for the experiments carried out at 300 and 400 °C (Fig. 1b and c). At 500 °C the total amount of irreversibly adsorbed H₂S is even more than 1 mmol/g. However, even for these experiments, a pseudo steady state is reached after about 10 cycles and the amount of H₂S irreversibly adsorbed then even becomes smaller than what was observed at 400 °C (green bars in Fig. 1c and d). The cyclic steady state working capacity for all three operating temperatures is very similar (0.2 mmol/g) for the used experimental conditions (0.05 bar partial pressure of H₂S and a half-cycle time of 60 min). The cause for the observed differences on the pseudo steady state and the large amount of irreversibly adsorbed H₂S at 400 and 500 °C is related to differences in the adsorption rate.

Fig. 2a shows the weight change during the first adsorption cycle. For the first 50 s the adsorption rate is the same irrespective of the operating temperature. Then, a decrease in this fast adsorption rate occurs first for the experiment at 500 °C then for 400 and 300 °C. The second part is much slower at 300 °C, where nearly no H₂S is being adsorbed after first 250 s. At 400 °C a constant weight increase can still be observed, while at 500 °C H₂S is being adsorbed with a high rate till the end of the experiment. This indicates the coexistence of two different mechanisms being responsible for the H₂S adsorption. The first fast part of H₂S adsorption can be explained by a weak chemisorption, where at higher operating temperature

Fig. 1 – a) Weight change obtained in TGA at different operating temperatures for the adsorption with H₂S ($P_{H_2S} = 0.05$ bar) and desorption with N₂; **b-d)** Amount of adsorbed, desorbed and irreversibly adsorbed H₂S at different temperatures.

Fig. 2 – a) Adsorption kinetics for the first cycle after the pretreatment at different temperatures; **b)** adsorption kinetics of the last cycle (pseudo steady state) at different temperatures; **c)** desorption kinetics for the last cycle at different temperatures.

the sorbent reacts with H₂S. This reaction seems to have a high activation energy explaining the clear differences between the rates at 500 °C and 300 °C. It has been reported in the literature, that H₂S reacts with γ -Al₂O₃ and surface complexes like S²⁻, HS⁻ and physically adsorbed H₂S are transformed to different complexes at higher temperatures [24]. It has been proposed that, after adsorption of H₂S on the surface, the dissociation of H₂S into HS⁻ and H⁺ takes place, which can diffuse into the oxide lattice, and migration of lattice oxygen to the surface to form H₂O confirming two different sorption mechanisms on mixed metal oxides [19]. Fig. 2b and c shows the adsorption and desorption rates for the last cycle, where a pseudo steady state is virtually reached. The two different regimes of a very fast initial weak chemisorption mechanism

(first 50 s) and a relatively slow reaction-driven adsorption of H₂S (after 50 s) and can be clearly discerned. Interestingly, the two different mechanisms seem to balance each other out in such a way that the cyclic working capacity results are almost the same at different operating temperatures. Fig. 2c shows that the pseudo steady state has not yet been fully established at 400 °C, since the amount of H₂S desorbed is still somewhat lower compared to the amount of H₂S adsorbed in the previous step.

After the experiments the sorbent showed a change in color from white (before the experiment) to yellow after being exposed to H₂S (see Appendix Figure A.1 showing the sorbent material after experiment 2 at 400 °C and ten adsorption/desorption cycles). It has been reported that white γ -Al₂O₃

changes its color to yellow upon H_2S adsorption [24]. Interestingly, this change in color was reversible, when the sorbent was exposed to the atmosphere at room temperature for several hours, where H_2S could be detected based on the smell of the sorbent. XRD performed after the experiment could not reveal any crystalline phase upon H_2S adsorption, which in general is highly amorphous and therefore difficult to be analyzed with XRD. Sulfate formation upon the interaction with H_2S on alumina catalyst has been reported in the literature [25]. It has been reported that the reaction of H_2S with mixed metal oxides (involving formation of sulfides and sulfates) leads to the release of H_2O [19,20]. This reaction is reversible and seems to take place even at room temperature with H_2O being present in the atmosphere resulting in the formation of H_2S . Sulfuric species in the hydrotalcite structure can react with H_2O to form H_2S , which explains the strong odor of H_2S of the sorbent when exposed to the atmosphere.

Mechanism for H_2S adsorption on KGM30: interaction between H_2S and H_2O

TGA and packed bed reactor experiments

In the following section, TGA and breakthrough experiments using the packed bed reactor will be presented together to explain the sorption mechanism involving different adsorption sites on the sorbent and to analyze the capacity of these different adsorption sites. The TGA results show results for two different H_2S concentrations. The height of the arrow used in the figures represents the actual cyclic working capacity of a certain adsorption site within one cycle. Fig. 3a shows the adsorption of H_2S and the regeneration with N_2 at 400°C and a partial pressure of 0.02 and 0.03 bar H_2S respectively (experiment 2, Table 2). The cyclic working capacity of this adsorption site (called B like for CO_2 in a previous publication) increases slightly when increasing the H_2S partial pressure reaching about 0.2 mmol/g at 0.03 bar for a half-cycle time of 30 min. Breakthrough curves (Fig. 3b) confirm the results of the TGA experiments. During adsorption, a small temperature increase of a few degrees C can be observed that moves along the bed with the adsorption front. Note that this experiment represents the fifth cycle (TGA) and the second

cycle of the PBR. The sorbent was exposed previously to H_2O (EXP1, Table 2).

The interaction between H_2S and H_2O within one cycle was studied with experiment 3. Note that in Fig. 4a the sorbent is loaded with H_2S (same state as at the end of experiment 2, Fig. 3a, step1). The presence of a second adsorption site for H_2S , which can be regenerated with H_2O , leading to an increase in the cyclic working capacity of the sorbent can be confirmed. Based on the TGA experiments, the capacity of this site has been determined at 4.66 and 6.44 mg/g at 0.02 bar and 0.03 bar H_2S , respectively. In terms of H_2S capacity, this would mean about 0.46 and 0.64 mmol/g for an equimolar exchange of H_2S by H_2O and vice versa. It has been reported that H_2S can dissociatively adsorb on $\gamma\text{-Al}_2\text{O}_3$ with H_2O formation according to the following equation [24,26,27],

where [O] and [S] represents oxygen -or sulfur species at the surface respectively. Another pathway, including the formation of metal sulphide upon exposure to H_2S and partial backformation of the metal oxide under exposure to steam, has been suggested in the literature according to Eq. (2) [18,28].

If the sorbent is exposed to H_2O this reaction mechanism can be reversible. Site A (for H_2O) was introduced in an earlier publication and represents a sorption site being only available for H_2O which can be regenerated with N_2 [13]. Breakthrough curves plotted in Fig. 4b confirm the observations in the TGA experiments. Moreover, the observed temperature increase in the reactor during the adsorption of H_2O is higher compared to the temperature increase during adsorption of H_2S . Desorption of H_2O (regeneration with N_2 in step 3) leads to a decrease in the reactor temperature due to the endothermic desorption of H_2O . From the TGA experiments it was observed that the weight loss during the last regeneration cycle is higher than expected if only steam from site A would desorb. It was proven with an additional experiment (Fig. 4c) that the somewhat higher weight loss is caused by H_2S still being desorbed during

Fig. 3 – Adsorption -and desorption cycle (30 min half-cycle time) for H_2S at 400°C on KMG30: a) TGA experiment with 0.02 bar -and 0.03 bar of H_2S ; b) Packed bed reactor experiments with 0.03 bar of H_2S .

Fig. 4 – a) TGA experiment 3400 °C with $P_{\text{H}_2\text{S}} = 0.03$ bar and $P_{\text{H}_2\text{O}} = 0.034$ bar; b) PBR experiment 3 with $P_{\text{H}_2\text{S}} = 0.03$ bar and $P_{\text{H}_2\text{O}} = 0.1$ bar; c) 5 adsorption cycle of H₂S regenerated with N₂ followed by 10 adsorption cycles of H₂O, regenerated with N₂.

the regeneration steps. It can also be seen (due to the constant weight change afterwards), that only the first 30 min are affected by desorption of H₂S. In order to account for the additional weight loss in the last experiment an adsorption site D is introduced in the later described model to predict weight changes obtained by TGA (which capacity will be ~2 mg/g according to Fig. 4a).

The molar replacement ratio between H₂S and H₂O (site C) was determined based on breakthrough experiments in the packed bed, ranging between 0.81 and 1.46, which is similar to the replacement ratio for CO₂ (0.97–1.33). Because the molar replacement ratio is influenced by the transient behavior of the packed bed reactor and both adsorption and desorption kinetics are different for the binary mixtures (CO₂ and H₂O, H₂S and H₂O) a direct comparison is not possible. The ratio between the different adsorption sites B and C was determined based on both TGA and packed bed reactor experiments and are shown in Table 3. According to the TGA experiments, a higher H₂O concentration can increase the capacity of adsorption site C. In general, despite the very different partial pressures of CO₂ compared to H₂S, the ratio between the adsorption sites B and C remains similar between 0.81 and 1.46.

Adsorption site C has shown a dependency on the partial pressure of the interacting sorbate species for the CO₂/H₂O binary sorbate system [11]. Experiments 4 and 5 were used to determine the existence of any competition between the sorbate species H₂O and H₂S on site C. Fig. 5 shows the results of these experiments, where the partial pressure of H₂S was kept constant in the first two steps and the partial pressure of H₂O has been increased (Fig. 5a and b, TGA, PBR) or decreased

(Fig. 5c and d, TGA, PBR). Any change in partial pressure of H₂O will lead to either desorption of H₂S (Fig. 5a and b) due to partial replacement of H₂S from adsorption site C or to additional adsorption of H₂S (Fig. 5c and d) because more sites become available for H₂S, if the partial pressure of H₂O is lowered. These findings can be explained by incorporation of H₂S into the mixed metal oxide structure, which usually leads to the formation of H₂O [24,26,27]. If the partial pressure of H₂O is not equal to zero, formation of H₂O on the surface of the sorbent could be hindered, preventing further adsorption of H₂S. Like previously demonstrated for the sorbate interaction between H₂O and CO₂, feeding both H₂S and H₂O to the sorbent increases the cyclic working capacity of site C (therefore called site C*). A reason for this behavior could be a more effective regeneration or an increase in basic surface sites, when H₂O is present on the sorbent surface during H₂S adsorption. However, this behavior can only be highlighted by TGA experiments. The transient behavior of the packed bed reactor makes it difficult to discern this effect, since it is obscured by other effects like re-adsorption of some H₂S along the bed, because only the very first part of the bed can be regenerated in these experiments. Capacities of site C for a mixed feed of H₂S and H₂O (called C_{eq}) was determined based on the TGA experiments at 1.06 and 3.82 mg/g weight change, which corresponds to 0.106 and 0.382 mmol/g H₂S capacity, when assuming an equimolar exchange between H₂S and H₂O.

Regeneration of the sorbent by lowering the partial pressure of H₂S and keeping the H₂O partial pressure constant was investigated with experiment 7. It was found that the proposed model with sites A, B and C can describe the measured

Table 3 – Ratio between adsorption site C and B for TGA and PBR experiments at 400 °C and atmospheric pressure at different conditions for both CO₂ and H₂S.

H ₂ S/H ₂ O - TGA		CO ₂ /H ₂ O - TGA		H ₂ S/H ₂ O - PBR		CO ₂ /H ₂ O - PBR	
Conditions	C/B	Conditions	C/B	Conditions	C/B	Conditions	C/B
2% H ₂ S, 10% H ₂ O	0.81	20% CO ₂ , 34% H ₂ O	1.24	3% H ₂ S, 10% H ₂ O	1.19	20% CO ₂ , 10% H ₂ O	1.51
2% H ₂ S, 20% H ₂ O	1.27	40% CO ₂ , 34% H ₂ O	1.46			20% CO ₂ , 20% H ₂ O	1.22
2% H ₂ S, 34% H ₂ O	1.22	60% CO ₂ , 34% H ₂ O	1.11			30% CO ₂ , 20% H ₂ O	0.96
3% H ₂ S, 34% H ₂ O	1.21	66% CO ₂ , 10% H ₂ O	1.02			2.5% CO ₂ , 10% H ₂ O	1.56

Fig. 5 – a) TGA experiment 4 at 400 °C with $P_{\text{H}_2\text{S}} = 0.03$ bar and $P_{\text{H}_2\text{O}} = 0.034$ bar; b) PBR experiment 4 with $P_{\text{H}_2\text{S}} = 0.03$ bar and $P_{\text{H}_2\text{O}} = 0.1$ bar; c) TGA experiment 5 at 400 °C with $P_{\text{H}_2\text{S}} = 0.03$ bar and $P_{\text{H}_2\text{O}} = 0.034$ bar; d) PBR experiment 5 with $P_{\text{H}_2\text{S}} = 0.03$ bar and $P_{\text{H}_2\text{O}} = 0.1$ bar.

weight change of the TGA experiment (Fig. 6a). Breakthrough results show that there is no difference between a dry sorbent (Fig. 6b) and a wet sorbent (Fig. 6c), confirming that site A for water is completely independent from site C (confirming our proposed mechanism for H₂S–H₂O interaction on KGM30).

Influence of partial pressure and operating temperature on cyclic working capacity

The cyclic working capacity of the different adsorption sites at different partial pressures of H₂S and H₂O was determined from the TGA experiments and the results are plotted in Fig. 7a. Increasing the partial pressure of H₂O leads to an increase in the cyclic working capacity for site A. The influence of the H₂O partial pressure on the cyclic working capacity of site C is not very clear. One has to notice that the plotted cyclic working capacities are determined by fitting the cyclic working capacities to simulate the obtained weight change in the TGA (in terms of weight change per step as already published

in detail elsewhere [13]). A possible explanation for the strong variation in the cyclic working capacity of site C and C_{eq} at 400 °C and $P_{\text{H}_2\text{O}} = 0.2$ bar could be related with the experimental error and sensitivity to the fitting, which could lead to a different combination of cyclic working capacities of the different sites describing the experimental results best. The deviation between the predicted weight change for each experiment by the model and the experimental results can be found in the Appendix (Table A.1). In general, one would expect a positive influence of a higher partial pressure of H₂O on the cyclic working capacity of site C, since more H₂S can be replaced in the same time. Site B and D are not affected by any change in the H₂O partial pressure, which is expected since site D represents just the insufficient desorption time for site B and should in general be independent of the H₂O partial pressure. An increase in the partial pressure of H₂S leads to an increase in the cyclic working capacity of both sites B and C, as expected. The influence of the operating temperature was

Fig. 6 – a) TGA experiment 7400 °C with $P_{\text{H}_2\text{S}} = 0.03$ bar and $P_{\text{H}_2\text{O}} = 0.034$ bar; b) PBR experiment 7 with $P_{\text{H}_2\text{S}} = 0.03$ bar and $P_{\text{H}_2\text{O}} = 0.1$ bar cycle 1; c) PBR experiment 7 with $P_{\text{H}_2\text{S}} = 0.03$ bar and $P_{\text{H}_2\text{O}} = 0.1$ bar cycle 2.

studied with packed-bed reactor experiments and the results are shown in Fig. 7b. The cyclic working capacity of site A is higher at lower temperatures, whereas the cyclic working capacity of H₂S is decreased. This leads to the conclusion that the cyclic working capacity of the sorbent for H₂S is increased by operation at higher operating temperatures, if the regeneration is carried out with steam.

The influence of H₂ on the adsorption behavior and kinetics of H₂S was studied during in a separate experiment (experiment 4, Table 1). Fig. 8 shows the weight change during the TGA experiments 1–8 according to Table 2 with a constant H₂ partial pressure of 0.025 bar (black) and without H₂ (red, experiments as described in the previous figures). For the experiment without H₂, a continuous increase in weight is observed (probably related to H₂S irreversible bond to the sorbent, as described in section Adsorption and desorption of

H₂S at different operating temperatures). Presence of H₂ seems to hinder the irreversible adsorption of H₂S completely, where the cyclic working capacity remains unchanged over many cycles. This is an important finding regarding the aging and probably the long-term stability of the sorbent when used for H₂S adsorption in a continuous process. It was tested whether H₂ can also hinder the irreversible adsorption of CO₂ observed during earlier studies [12,13]. However, no significant effect of H₂ on the adsorption behavior of CO₂ was found.

mechanism for H₂S adsorption on KGM30: interaction between H₂S and CO₂

The same approach was used to investigate the interactions of CO₂ and H₂S using experiments 8 (TGA) and 11–13 (PBR). In general, the experiments can be described with four

Fig. 7 – a) Cyclic working capacities determined with the model to describe the weight changes during TGA experiments at 400 °C; b) cyclic working capacity of different sorption site determined during packed bed reactor experiments (average of adsorption and desorption capacity of a certain adsorption site).

Fig. 8 – TGA experiment at 400 °C with $P_{H_2S} = 0.03$ bar and $P_{H_2O} = 0.34$ bar with (0.025 bar of H_2) and without H_2 .

adsorption sites, where differences and similarities to the mechanism introduced for the system H_2S and H_2O will be pointed out in the next section. Fig. 9 shows the results of the first two breakthrough experiments with consecutive cycles containing either H_2S or CO_2 at 400 °C after the pretreatment. Where the regeneration step shows the same kinetics and capacity for CO_2 , it can be observed that during the adsorption of CO_2 , H_2S is being desorbed from the sorbent and the breakthrough time for CO_2 is shorter than that what was reported in an earlier publication for the system H_2O and CO_2 . The pretreatment procedure (N_2 flow at 600 °C for 120 min) is apparently insufficient to desorb all the H_2S from the sorbent. Also, the results of the TGA experiments where it was observed that H_2S reacts strongly with the sorbent at higher operating temperatures, indicated that the chosen pretreatment method may not be sufficient for H_2S (if the same material is used in a second experiment like PBR experiments). The replacement of H_2S by CO_2 seems to be also rather slow, since in the second cycle the sorbent is still releasing H_2S .

In contrast to CO_2 that can replace H_2S , replacement of CO_2 was hardly observed during adsorption experiments with H_2S (Fig. 10). Only a small breakthrough of some CO_2 was detected together with the breakthrough of H_2S . The cyclic working

capacity and breakthrough time were very similar to those of experiment 9 (Table 1), shown in Fig. 3b, which indicates that the sorbent does not seem to lose its capacity over multiple experiments also for H_2S .

With experiment 3 it is demonstrated that the cyclic working capacity can be increased for both sorbate species, if the regeneration with the competing sorbate species on adsorption site C is combined in one experiment (see Fig. 11). It was found that the H_2S capacity of site C is increased compared to a similar experiment with H_2O . It seems that the competing sorbate has a large influence on the capacity of the remaining sorbate in cyclic operation. The ratio between the capacity of adsorption sites B and C for the system H_2S/CO_2 , calculated to be between 2.08 and 2.71, is significantly higher in comparison to 1.19 if H_2O was used as competing sorbate on site C, even though the partial pressure of CO_2 is lower in comparison to the H_2O experiments (0.05 bar compared to 0.1 bar). Both experiments show that during step 3 (CO_2) the replacement of H_2S is not yet complete, which indicates that the theoretical capacity of site C can be very high. Slower kinetics of CO_2 replacing H_2S compared to the H_2O/H_2S interaction is confirmed by the TGA experiments (see Appendix, Figure A.2), which causes slip of H_2S at the end of step 3, as also shown in Fig. 12a and b. Interestingly, the replacement of CO_2 by H_2S is much faster (Fig. 11, step 1), since the CO_2 signal is close to zero at the end of the step.

Competition of both sorbate species CO_2 and H_2S on site C was studied with experiments 4 and 5 (Table 2), and the results are shown in Fig. 12. As before, the partial pressure of H_2S was kept constant during the first two steps, while the partial pressure of CO_2 was changed. Again, partial replacement of H_2S (Fig. 12a, step 2) and vice versa the partial replacement of CO_2 (Fig. 12b, step 2) is observed, however, with significant differences in their replacement kinetics. The breakthrough of H_2S occurs in two steps: if CO_2 is breaking through the bed, slip of H_2S is observed (in a low concentration of about 0.8%), which remains constant until total breakthrough of H_2S . It was demonstrated with a TGA experiment (Appendix, Figure A.3) that indeed the replacement of CO_2 and H_2S is very slow, when the sorbent is exposed to both CO_2 and H_2S in a single step. The competitive adsorption behavior of H_2S and CO_2 has also been mentioned in the past by other researchers, It was suggested that surface species such as carbonates (CO_3^{2-} and HCO_3^-) and thiocarbonate (SCO_3^- and $HSCO_2^-$) maybe formed onto the sorbent surface [18,29].

Fig. 9 – Breakthrough experiment 1 of CO_2 and H_2S on KGM30 at 400 °C with $P_{CO_2} = 0.05$ bar and $P_{H_2S} = 0.03$ bar: a) cycle 1; b) cycle 2.

Fig. 10 – Breakthrough experiment 2 of CO₂ and H₂S on KGM30 at 400 °C with $P_{\text{CO}_2} = 0.05$ bar and $P_{\text{H}_2\text{S}} = 0.03$ bar: a) cycle 1; b) cycle 2.

Fig. 11 – Breakthrough experiment 3 of CO₂ and H₂S on KGM30 at 400 °C with $P_{\text{CO}_2} = 0.05$ bar and $P_{\text{H}_2\text{S}} = 0.03$ bar a) cycle 1 b) cycle 2.

Experiment 7 confirmed these results, where only the partial pressure of one sorbate species is lowered to zero within one cycle (CO₂ in this case). Both PBR (Fig. 13a) and TGA (Fig. 13b) experiments show slip of H₂S in the breakthrough experiments and the slow weight change during TGA measurements as a result of the slow replacement kinetics. Fig. 13b nicely illustrates that the weight change during TGA experiments can be divided into two different kinetic regimes, corresponding to the results found in the breakthrough experiments.

Mechanism for H₂S adsorption on KGM30: interaction between H₂S, CO₂ and H₂O

Adsorption and desorption of H₂S, CO₂ and H₂S was studied by keeping the partial pressure of one sorbate constant and changing the partial of the other sorbates to zero, one at a time. Fig. 14a and b shows the results of the packed-bed breakthrough experiments where the partial pressure of H₂O was kept constant. Figure a always show the first cycle and Figure b the second cycle. During the first step in Fig. 14a, all

Fig. 12 – a) Breakthrough experiment 4 of CO₂ and H₂S on KGM30 at 400 °C with $P_{\text{CO}_2} = 0.05$ bar and $P_{\text{H}_2\text{S}} = 0.03$ bar; b) Breakthrough experiment 5 of CO₂ and H₂S on KGM30 at 400 °C with $P_{\text{CO}_2} = 0.05$ bar and $P_{\text{H}_2\text{S}} = 0.03$ bar.

Fig. 13 – a) Breakthrough experiment 7 of CO₂ and H₂S on KGM30 at 400 °C with $P_{\text{CO}_2} = 0.05$ bar and $P_{\text{H}_2\text{S}} = 0.03$ bar; b) TGA Experiment 7 of CO₂ and H₂S on KGM30 at 400 °C with $P_{\text{CO}_2} = 0.05$ bar and $P_{\text{H}_2\text{S}} = 0.03$ bar.

components are adsorbed, where part of the adsorbed H₂S is directly replaced by CO₂ (desorption of some H₂S and adsorption of more CO₂), indicating a higher affinity of CO₂ towards the sorbent than H₂S. In the second step the partial pressure of H₂S is reduced to zero and H₂S is desorbed and replaced by CO₂ and H₂O. In this case, site C is fully occupied by both CO₂ and H₂O in a ratio depending on their partial pressures. A larger amount of CO₂ is adsorbed compared to H₂O caused by the intense competition of CO₂ and H₂S. In step 3, the H₂S partial pressure was increased again and the CO₂ partial pressure was reduced to zero. Both desorption of CO₂ and H₂O can be seen during the H₂S re-adsorption on adsorption sites B and C. The small adsorption peak of H₂O and the very high concentration peak of CO₂ in the beginning of step 3 can be attributed to the rapid exchange of H₂O on site C replacing CO₂. In Fig. 14b (step 1) the partial pressure of CO₂ is increased. As expected H₂S is replaced by CO₂ (desorption of H₂S) and part of H₂O (first sharp desorption peak) is replaced by CO₂. Interestingly, the adsorption of H₂O is taking place during the adsorption of CO₂. It seems that the adsorption of H₂O is favored when CO₂ is present on the adsorbent. The formation of hydroxide carbonate on the sorbent could be a possible explanation for the observed behavior, which has also been reported before using in-situ infrared [30] and in other works [9,31]. Fig. 14c and d shows the experimental results for a constant partial pressure of CO₂. The breakthrough curves during steps 1 and 2 are basically the same as shown in Fig. 14b confirming the reproducibility and stable adsorption behavior of the sorbent. In step 3 (Fig. 14c and d) the shape of the breakthrough curve is similar as observed in Fig. 14a and b, where the signal for CO₂ and H₂O is reversed as expected. In step 1 of Fig. 14d it can be observed that H₂S is again replaced by H₂O when increasing the H₂O partial pressure. Also, in this case, the adsorption of CO₂ indicates that the formation of hydroxide carbonate may take place. This hypothesis is confirmed by step 2 in Fig. 14e and f, where the desorption of H₂O induces the desorption of CO₂ (corresponding to the decomposition of the previously formed hydrogen carbonate), where normally one would expect a replacement on site C of H₂O by CO₂ (resulting in additional adsorption of CO₂). The free sites upon hydrogen carbonate decomposition seem to be occupied by H₂S in this experiment. If the partial pressure of

CO₂ is lowered as in step 3 of Fig. 14e and f, first H₂O seems to rapidly replace some CO₂ followed by a slow replacement (which confirms the earlier findings in this study of slow H₂S/CO₂ replacement kinetics), which is even not yet finished at the end of the cycle. Quantitative analysis of the experiment was carried out, except for step 1 of each experiment because the H₂S concentration was above the maximum readout of the H₂S analyzer (5%) and indicates that equimolar exchange seems to take place on the sorbent. This implies that there is no separate adsorption site for H₂S, since otherwise one would expect during experiments a2, b2, c2 and d2 a higher amount of H₂S being desorbed than the amount of H₂O and CO₂ already adsorbed. Some authors have reported that H₂S does not seem to be regenerated from a hydrotalcite-based adsorbent if the CO₂ partial pressure is decreased and steam is used for regeneration [17]. Note that in their study the used partial pressure of H₂S was much lower (about 430 ppm) and the regeneration temperature was higher (500 °C). We have shown that H₂S seems to chemisorb stronger at higher temperatures which could be the reason why H₂S was remaining on the sorbent at the regeneration conditions used in their study.

It has previously been reported that the three sorbate species are competing depending on their basicity on the sorbent. The influence of the partial pressure is studied in additional experiments (see Fig. 15a and b) where all sorbate species are present on the adsorbent. The partial pressure of H₂S was kept constant during all these experiments. In Fig. 13a the partial pressure of CO₂ was increased and decreased stepwise. For increasing CO₂ partial pressures, H₂S and H₂O are being desorbed. However, the replacement is more evident for H₂S than for H₂O, confirming the strong competition between CO₂ and H₂S on adsorption site C. The effect is smaller for the change between 0.15 and 0.2 bar compared to 0.1–0.15 bar. This exchange is reversible if the CO₂ partial pressure is lowered, for both H₂S and H₂O. An increase in the H₂O partial pressure (Fig. 13b) leads to the desorption of H₂S and slightly of CO₂. The exchange with H₂O is somewhat slower compared to the exchange with CO₂, which can be related to differences in their concentrations (slower adsorption/desorption fronts through the reactor bed). This experiment confirms our hypothesis, that CO₂ has the highest affinity to the sorbent (highest basicity) and is therefore able to replace more H₂S, compared to H₂O.

Fig. 14 – Packed bed reactor experiments with H₂S, CO₂ and H₂O at 400 °C $P_{\text{CO}_2} = 0.05$ bar, $P_{\text{H}_2\text{S}} = 0.03$ bar and $P_{\text{H}_2\text{O}} = 0.1$ bar: a & b) constant partial pressure of H₂O, c & d) constant pressure of CO₂, e & f) constant pressure of H₂S.

Fig. 15 – Packed bed reactor experiments with H₂S, CO₂ and H₂O at 400 °C a) $P_{\text{CO}_2} = 0.05\text{--}0.15$ bar, $P_{\text{H}_2\text{S}} = 0.03$ bar and $P_{\text{H}_2\text{O}} = 0.1$ bar b) $P_{\text{CO}_2} = 0.05$ bar, $P_{\text{H}_2\text{S}} = 0.03$ bar and $P_{\text{H}_2\text{O}} = 0.1\text{--}0.2$ bar.

Conclusions

The H₂S adsorption capacity and kinetics and the interaction between different sorbate species, viz. CO₂ and H₂O, were investigated up to 0.05 bar of H₂S on a commercial potassium-promoted hydrotalcite-based adsorbent. The sorbent has a high cyclic working capacity for H₂S, where the operating temperature during adsorption has a large influence on the adsorption behavior. A higher temperature (500 °C) leads to high irreversible H₂S adsorption and the kinetics are very different compared to lower temperatures (300 °C), indicating that two different adsorption mechanisms are involved. The pretreatment method (600 °C and N₂) is insufficient to remove all adsorbed H₂S. This can be explained by the high irreversible H₂S adsorption detected due to a strong chemisorption mechanism with a high activation energy. The three-site model developed for CO₂ and H₂O was shown to be valid in general for all binary mixtures (CO₂/H₂O, H₂S/H₂O, CO₂/H₂S), where the cyclic working capacity of the sorbent can be significantly increased when another interacting sorbate is used for the regeneration, but not an inert component. This is an important observation for any type of process optimization using hydrotalcite-based adsorbents. Both CO₂ and H₂S seem to interact stronger with the sorbent than H₂O and replacement of CO₂ by H₂S and vice versa is much slower in comparison to the replacement with H₂O. In a ternary system, depending on the partial pressure, all sorbate species interact with the sorbent and an equimolar exchange can be expected between the sorbent species in a steady state operation. A small amount of H₂ in the feed stream can significantly reduce the irreversible interaction between H₂S and the sorbent, where the cyclic working capacity of the sorbent remains unchanged. This is a very important observation regarding the long-term stability of the sorbent for continuous H₂S adsorption processes. Therefore, KMG30 seems to be a very interesting and suitable sorbent for the desulfurization of flue gas. Depending on the partial pressure of sorbate species both CO₂ and H₂S are adsorbed on the sorbent and can be regenerated with H₂O. More detailed studies are required for different gas phase compositions to optimize the cyclic working capacity and regeneration conditions depending on the primary use of the sorbent such as CO₂ removal or H₂S removal from gas streams at elevated temperatures.

Acknowledgements

The research leading to these results has received support through the ADEM innovation lab program TUE-P05. Additionally, we would like to thank Christian di Stasi, Marian Palacino, Thijs van Raak and Mariela Villarreal Brito for their contribution to this publication.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ijhydene.2018.09.146>.

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