

Investigating the role of the different metals in hydrotalcite Mg/Al-based adsorbents and their interaction with acidic sorbate species

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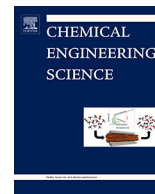
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Investigating the role of the different metals in hydrotalcite Mg/Al-based adsorbents and their interaction with acidic sorbate species



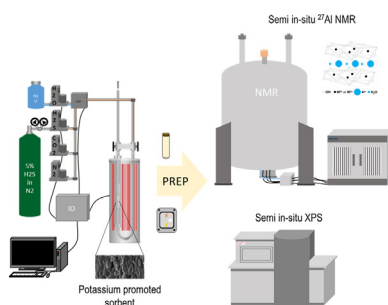
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HIGHLIGHTS

- Semi in-situ characterization was used to investigate the role of Al in hydrotalcite sorbents.
- The chemisorption of different sorbate species such as CO₂, H₂O and H₂S, was studied at High T.
- Samples were characterized with ²⁷Al-NMR and XPS under after reaction with sorbate species.

GRAPHICAL ABSTRACT



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ABSTRACT

The role of aluminum in the structure of hydrotalcite-based sorbents was investigated with ²⁷Al-NMR and XPS with respect to the chemisorption mechanism of different sorbate species, such as CO₂, H₂O and H₂S, at elevated temperatures. Sorbent materials with different ratios of Al/Mg were studied in order to elucidate the influence of the material composition on the Al coordination. Two different tetrahedrally and octahedrally coordinated Al species were detected. It was found that their quantitative appearance depends on the ratio of Al/Mg within the sorbent material. A higher Mg content leads to a higher distortion and to the formation of more tetrahedrally coordinated Al with a high chemical shift. Whereas CO₂ and H₂O adsorption does not seem to influence well-coordinated Al, as observed with NMR, chemisorption of H₂S showed a clear interaction with Al leading to the formation of an additional tetrahedrally coordinated site with a high chemical shift. XPS showed that a reversible metal sulfate complex was formed on the sorbent, which was reversible upon exposure to H₂O.

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1. Introduction

Mixed metal oxide (MMO) adsorbents derived from hydrotalcites are interesting materials for the use as catalysts and selective sorbents for acidic gases such as CO₂ and H₂S. The most common sorbents are based on hydrotalcites of MgO and Al₂O₃, which are usually impregnated with K₂CO₃ to increase the surface basicity. Usually the unit cell composition of the original Mg/Al hydrotalcite

is described before calcination as $[\text{Mg}_6\text{Al}_2(\text{HO})_{16}\text{CO}_3^{2-}] \times 4 \text{H}_2\text{O}$, where the atomic ratio between Mg/Al can vary for synthetic samples (Di Cosimo et al., 1998). Their application as sorbents for sorption-enhanced processes at elevated temperatures has been demonstrated in various prior publications (Cobden et al., 2007; Dragicevic and Ivarsson, 2013; Gallucci et al., 2015; Jang et al., 2012; Lu et al., 2013; Reijers et al., 2009; Selow et al., 2009; Wu et al., 2013). The influence of material composition (especially the variation in the MgO/Al₂O₃ content) and different preparation methods have been studied intensively by various researchers in the recent past (Cairon et al., 2007; Di Cosimo et al., 1998; Kim

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Nomenclature

Al _T	tetrahedrally coordinated aluminum	NMR	Nuclear Magnetic Resonance spectroscopy
Al _O	octahedrally coordinated aluminum	MMO	mixed metal oxide
HTC	hydrotalcite based material	XPS	X-Ray Photoelectron Spectroscopy
TGA	thermogravimetric analysis		

et al., 2016; Prescott et al., 2005; Sahoo et al., 2014; Wang et al., 2012). However, the interaction of the sorbent with acidic gas molecules and the role of the different metal ions present in the sorbent structure yet to be fully understood. X-ray diffraction can provide insight into the bulk structure of the sorbent but has no value for determining adsorption sites. Nuclear magnetic resonance (NMR) can be used to study the Al speciation in the parental and activated materials (Sideris et al., 2008). Generally, ²⁷Al-NMR and ¹H NMR are used to characterize the samples and structural changes upon thermal decomposition. In this study we investigated three different hydrotalcite-derived sorbents with different ratios of Mg/Al before and after thermal treatment. Since the sorbent will adsorb CO₂ and H₂O immediately from the atmosphere, the measurements were carried out in a quasi *in situ* manner in order to avoid contamination of the sorbent samples. We focused on the interactions of the sorbents with CO₂, H₂O and H₂S using both ²⁷Al-NMR and XPS.

1.1. Influence of material composition and adsorption behavior of sorbents

Hydrotalcite based sorbents with different ratios of Mg/Al and a potassium promoted alumina were described in previous reports (Coenen et al., 2018a, 2018c) to determine the adsorption behavior at different operating temperatures between 300 and 500 °C under exposure to H₂O, H₂S and CO₂. The focus was on finding the sorbent with the highest cyclic working capacity for CO₂, but also to understand the interaction of CO₂ with H₂O and H₂S in order to predict the sorption behavior for sorbate mixtures.

The cyclic working capacity of the sorbent is in general determined by the slow regeneration (desorption kinetics), which can be enhanced by operation at higher temperatures (Coenen et al., 2016). The presence of H₂O during the adsorption of CO₂ has different effects: First, co-adsorption of CO₂ and H₂O leads to an increase in the adsorption capacity (probably due to the formation of some bicarbonate species, which were detected with *in-situ* IR (Coenen et al., 2018d)). Secondly, CO₂ and H₂O compete depending on their partial pressure, which could lead to a replacement of CO₂ by H₂O when the partial pressure of H₂O is increased (Coenen et al., 2017). This competition of CO₂ and H₂O results in an enhanced regeneration of the sorbent. The regeneration capacity of CO₂ can therefore be improved significantly by using steam instead of an inert such as N₂. In Fig. 1 we show the effect of regeneration on the breakthrough time (hence adsorption capacity for CO₂), which was determined with packed-bed reactor experiments using KMG30 as a sorbent with identical time (1 h) for regeneration. The breakthrough time for CO₂ is about twice as long, when the sorbent was regenerated with steam (red¹ dotted line) compared to the regeneration with N₂ (red line), and consequently more CO₂ is regenerated if steam is used during the experiment. This implies that the cyclic working capacity can be at least doubled when using steam during the regeneration.

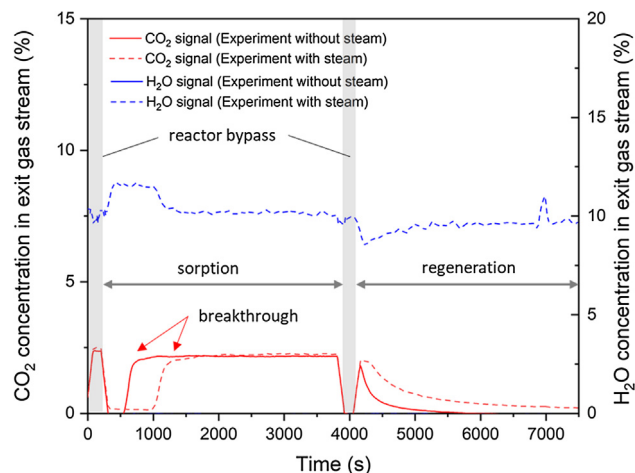


Fig. 1. Breakthrough experiment in a packed-bed reactor with KMG30 as sorbent at 400 °C and $P_{\text{CO}_2} = 0.025$ bar and $P_{\text{H}_2\text{O}} = 0.1$ bar with 1 h regeneration step. Detailed description of experiments and experimental setup can be found elsewhere (Coenen et al., 2017).

To describe the adsorption behavior of a binary mixture such as combination of CO₂ and H₂O, or H₂S and H₂O, a phenomenological model was developed considering different adsorption sites. Weaker bond sorbate can be easily regenerated with N₂, while a stronger bond sorbate requires the replacement with a competing sorbate species. Therefore, we need at least three adsorption sites to describe the interaction of any binary sorbate mixture with the adsorbent. Two sites for each component representing the weaker bond sorbate and one site describing the exchange of one sorbate by the other. The cyclic working capacities of the different adsorption sites seem to be strongly dependent on the chemical composition of the sorbent. Sorbent materials with a high content of MgO (such as KMG70, Table 1) show a higher concentration of adsorption sites for CO₂ which can be regenerated with N₂ compared to the other sorbents. Sorbent material with a high Al₂O₃ content (such as KSORB, Table 1) show a higher cyclic working capacity for the exchange site (e.g. CO₂ replacing H₂O and vice versa) (Coenen et al., 2018c). From this observation one may conclude that Al₂O₃ in combination with K₂CO₃ impregnation seem to be mainly responsible for the exchange site, whereas the MgO content in the sorbent structure seems responsible for the adsorption site which can be regenerated with an inert (e.g. N₂). KMG30 showed the highest cyclic working capacity for CO₂ and the highest chemical stability and is therefore the most promising sorbent which we have investigated so far (Coenen et al., 2018a, 2018c). Additionally, this sorbent shows a high sorption capacity for H₂S which can be used for the desulfurization of gas streams (Coenen et al., 2018b). This sorbent was selected to study interaction with sorbates such as CO₂, H₂O and H₂S with semi *in situ* NMR and XPS which will be discussed in this publication.

¹ For interpretation of color in Figs. 1 and 6, the reader is referred to the web version of this article.

Table 1
Material compositions of different sorbent materials used for this work.

Material	Mg/Al atomic ratio	Al/K	Mg/K	K ₂ CO ₃ wt%
KSORB	–	5.42	–	20
KMG30	0.54	3.79	2.06	20
KMG70	2.95	1.63	4.80	20

2. Materials & methods

A potassium-promoted hydrotalcite-based adsorbent, with a Mg/Al ratio of 2.95 (KMG70) and a potassium-promoted alumina (KSORB) were used in this work and compared to a potassium-promoted hydrotalcite-based adsorbent with a Mg/Al ratio of 0.54 (KMG30). Table 1 shows the material composition of the different sorbent materials that were investigated in the past for their use in sorption-enhanced water gas-shift reaction (SEWGS). The commercial materials were pre-calculated by the manufacturer (SASOL) at 250 °C and 450 °C for 24 each hours (Maroño et al., 2013).

Both 1D and 2D ²⁷Al-NMR spectra were recorded from a fresh sample and a pretreated sample of all materials mentioned in the Table 1. Pretreated means heating up the sorbent material to 600 °C with a heating ramp of 10 °C/min and a dwell time of 120 min continuously feeding N₂ to the sorbent material to release adsorbed and chemisorbed H₂O and CO₂ (Coenen et al., 2016).

Gas adsorption experiments were conducted for KMG30, as this material showed the highest cyclic working capacity for CO₂ and the highest chemical stability, which are both important parameters for its use in a SEWGS process (Coenen et al., 2018c, 2018a). Experiments were carried out in a small stainless-steel reactor with two valves. The powder (average particle size roughly 40 μm) was placed in a sample basket for TG experiments inside a 12 mm Swagelok tube. A platinum wire is attached to the upper socket and connected to the basket (see Fig. 2). After the reaction, the reactor was purged with N₂ and cooled to ambient temperature under a N₂ atmosphere. Afterwards, the inlet -and exit valves were

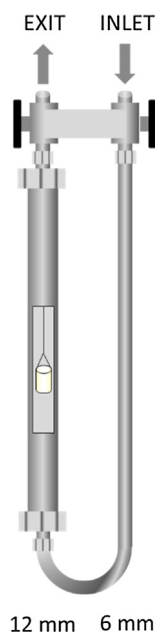


Fig. 2. Small test reactor for sample treatment under reactive atmosphere.

Table 2

Overview of the different semi-*in situ* experiments and the used characterization techniques on KMG30 treated with different gases ($P_{\text{CO}_2} = 0.66$ bar, $P_{\text{H}_2\text{O}} = 0.34$ bar, $P_{\text{H}_2\text{S}} = 0.03$ bar, temperature was 400 °C during the treatment; step duration was 30 min for each reaction step).

Exp. number	Treatment	XPS	²⁷ Al-NMR
1	Pretreatment with N ₂	X	X
2	CO ₂ → N ₂	X	X
3	CO ₂ → H ₂ O → N ₂	X	X
4	H ₂ O → N ₂	X	X
5	H ₂ S → N ₂	X	X
6	H ₂ S → H ₂ O → N ₂	X	X
7	H ₂ O → CO ₂ → N ₂		X
8	H ₂ O → CO ₂ → H ₂ O → N ₂		X
9	H ₂ S → N ₂ (hydrated in air)		X

closed, the reactor was removed from the test rig and transported to a glovebox (containing the sample under N₂ atmosphere). While continuously monitoring the H₂O (<1 ppm) and O₂ (<3 ppm) concentrations, the sorbent was removed from the reactor and samples were prepared for both NMR or XPS in the glovebox. Sorption experiments were carried out at 400 °C with identical conditions as described in previous TGA experiments with $P_{\text{CO}_2} = 0.66$ bar, $P_{\text{H}_2\text{S}} = 0.03$ bar and $P_{\text{H}_2\text{O}} = 0.34$ bar. An overview of the different experiments carried out in this work is provided in Table 2.

XPS measurements were carried out with a Thermo Scientific K-Alpha, with a monochromatic small-spot x-ray source and a 180° double focusing hemispherical analyzer. Spectra were obtained using an aluminum anode (Al K α = 1486.6 eV) operating at 72 W and a spot size of 400 μm. Survey scans were measured at a constant pass energy of 200 eV and region scans at 50 eV. Data analysis was performed using Casa XPS software. The binding energy was corrected for surface charging by taking the C1s peak of adventitious carbon as a reference at 284.6 eV. The samples were prepared in a glovebox in a closed sample holder to avoid any contamination with O₂ and H₂O during transport to the XPS.

Al-NMR experiments were performed in a Bruker Avance DMX500 operating at 132 MHz for ²⁷Al in a magnetic field of 11.7 Tesla. The measurements were carried out using a 2.5-mm MAS probe head with a sample rotation rate of 25 kHz. ²⁷Al 1D spectra were recorded with a single pulse sequence with a 18° pulse duration of 1 μs and an interscan delay of 1 s. MQMAS spectra were recorded by use of a pulse sequence p1-t1-p2-τ-p3-t2 for triple quantum generation and zero-quantum filtering (strong pulses p1 = 3.4 μs and p2 = 1.4 μs at ν1 = 100 kHz; soft pulse p3 = 11 μs at ν1 = 8 kHz; filter time τ = 20 μs; interscan delay 0.2 s). The ²⁷Al chemical shift is referred to a saturated Al(NO₃)₃ solution. The different samples were loaded in a 2.5-mm zirconia NMR rotor in a glovebox and closed with Kel-F cap. Afterwards, the rotor was transported to the NMR probe head under N₂ atmosphere.

3. Results and discussion

The following section consists of different parts. In the first part we summarized some important parts of the work previously conducted on hydrotalcite based adsorbents with an explanation of the importance of XPS and ²⁷Al-NMR in this report. In the second section we will focus on the different types of sorbents which were investigated upon heat treatment, because sorbent, used for adsorption test is usually treated at high temperature to release CO₂ and H₂O from the sorbent. In the third section we describe results based on semi *in situ* analysis of sorbent exposed to different gases such as CO₂, H₂O and H₂S.

3.1. Heat treatment of different sorbents

3.1.1. Al-NMR on fresh and pretreated sorbents

In the first part, we discuss the Al coordination in different sorbent materials and the changes upon heat treatment. In Fig. 3, 1D and 2D ^{27}Al -NMR spectra are plotted for the three different sorbents before and after pre-treatment. All sorbents contain Al in two different coordination environments as demonstrated by the 1D NMR spectra (Fig. 4). The peak at 9.5 ppm is characteristic for octahedrally coordinated Al (AlO_6) (Shylesh et al., 2016). The second broader resonance between 68 and 82 ppm can be assigned to tetrahedrally coordinated Al (AlO_4) (Corma et al., 1994; Guiyun and Lu-ming, 2015; Shylesh et al., 2016). Tetrahedral Al species are being formed during calcination of the exclusively octahe-

dral Al species in the original hydroxalcalite structure (Corma et al., 1994). The used parent material however, was already calcined by the manufacturer.

The broad tetrahedral peak in the KSORB sample before treatment consists of two overlapping peaks as can be seen from the 2D NMR spectrum (Fig. 3). After treatment, the two peaks merge into one very broad peak centered at intermediate chemical shift. The tetrahedrally coordinated Al in materials containing MgO shows a higher chemical shift in comparison to KSORB. The 2D spectra of the MgO containing samples (Fig. 3) show clearly the formation of a second tetrahedral coordination environment at higher chemical shift. The peak with the higher electron density (higher chemical shift) can be assigned to tetrahedrally coordinated Al in Al-O-Mg species, while the peak with lower electron

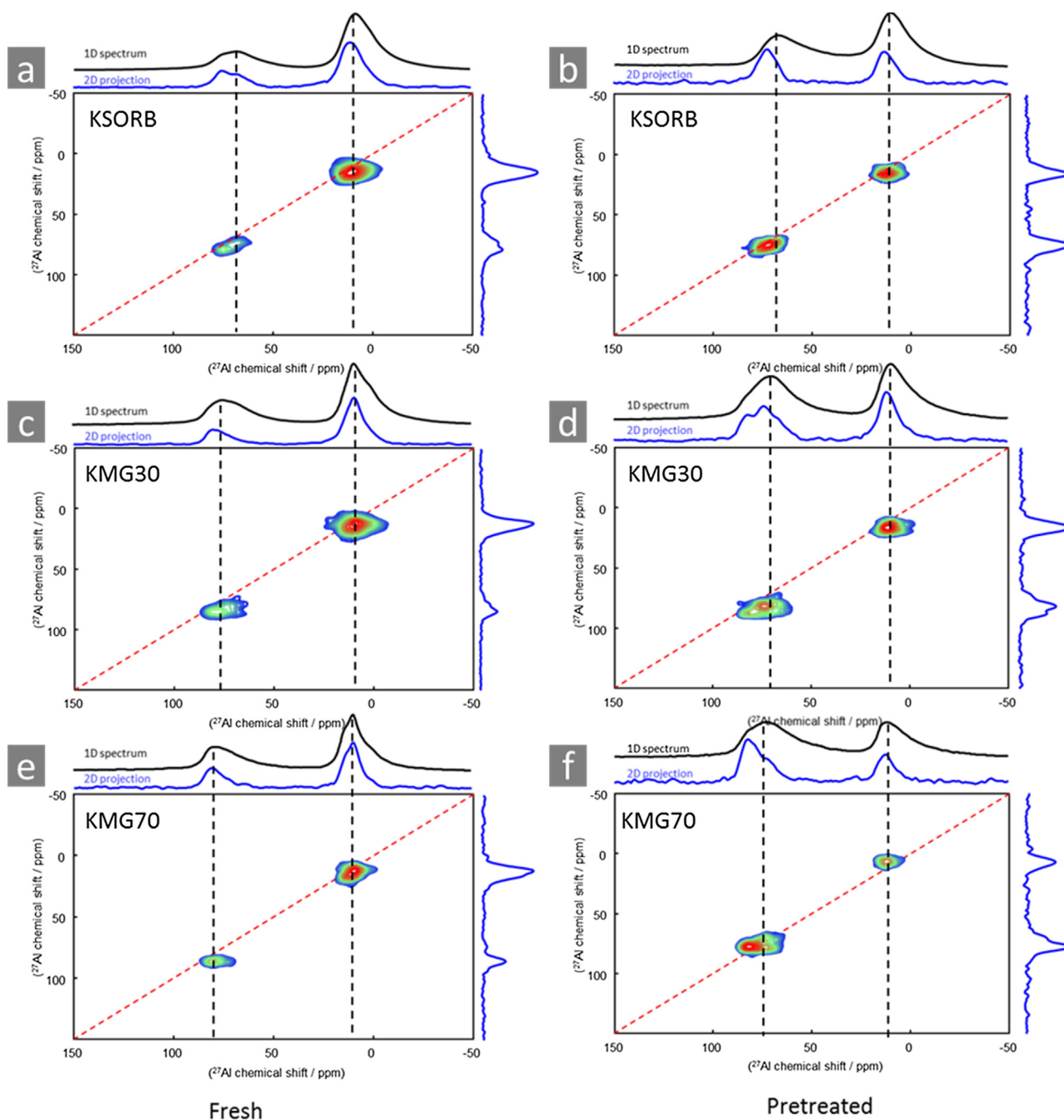


Fig. 3. 1D- and 2D ^{27}Al -spectrum of KSORB, KMG30 and KMG70.

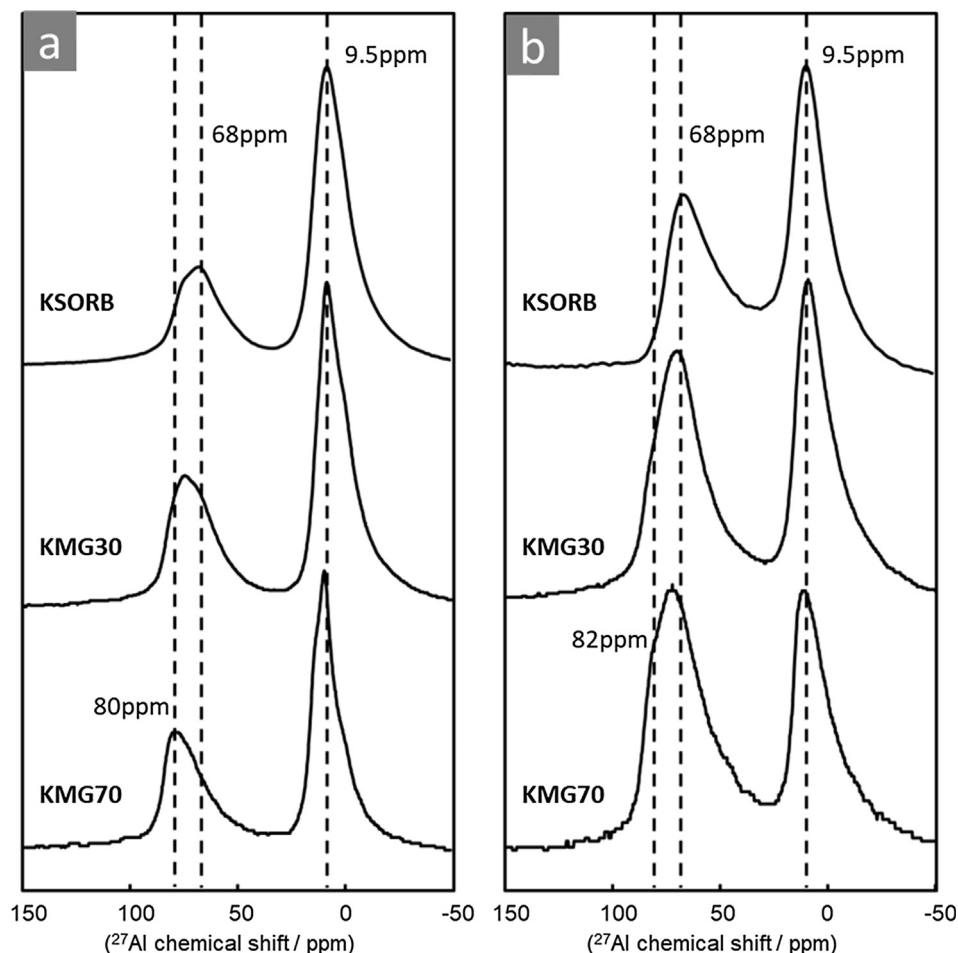


Fig. 4. ^{27}Al NMR spectra of KSORB, KMG30 and KMG70 before (a) and (b) after heat treatment.

density can be assigned to tetrahedral Al in Al-O-Al (Shen et al., 1998). The data shows that more Al-O-Mg species are formed on KMG70 than on KMG30, in line with the higher Mg content of the former. In principle, the calcination may lead to the formation of $\gamma\text{-Al}_2\text{O}_3$ but the $\text{Al}_\text{T}/\text{Al}_\text{O}$ ratios and the chemical shifts do not correspond with those expected for γ -alumina (Corma et al., 1994). The calcinated sorbents, (Fig. 3, right side) show that indeed the chemical shift of the Al_T are different for different Al/Mg ratios and are generally higher than for the K_2CO_3 promoted Al_2O_3 , but also higher than for unpromoted Al_2O_3 (65 ppm).

A comparison of the different materials before and after thermal treatment demonstrates that the amount of tetrahedrally coordinated Al increased during the thermal treatment for all materials. The difference is larger for materials with a higher Mg/Al ratio. For KMG70, the amount of tetrahedral Al exceeds that of octahedral Al after thermal treatment (Fig. 4). In MMO's derived from hydrotalcites a part of tetrahedral Al may be located at tetrahedral positions in the MgO lattice, which could lead to the formation of Mg-Al inverse spinel type (Corma et al., 1994). Within the same study was reported that with higher Al content the amount of tetrahedrally coordinated Al of calcined hydrotalcites increased. This is contrary to the results obtained within this study, where the amount of tetrahedrally coordinated Al becomes larger with increasing MgO content. Note that the lowest Mg/Al ratio in the cited study was about 2.33, which is much higher than the Mg/Al ratio of KMG30 (0.54). One explanation for this difference might be that there is an optimum Mg/Al ratio that results in a minimum formation of tetrahedral Al. Note that the sorbents in the men-

tioned study were not impregnated with K_2CO_3 . Therefore, also to mentioning that the presence of K may influence the Al distribution.

Incorporation of Mg in the Al-lattice cannot be the only reason for the formation of tetrahedrally coordinated Al as described in the literature. In our experiments we found tetrahedrally coordinated Al on potassium-promoted alumina (KSORB), where no Mg is present in the sorbent structure.

Integration of the normalized 1D spectrum of KMG30 revealed, that the amount of visible coordinated Al for NMR does not significantly improve upon heat treatment of the sample (Fig. 5). This implies that pre-treatment induces a transformation of octahedrally coordinated Al to tetrahedrally coordinated Al for this material. For KMG30, especially tetrahedrally coordinated Al (Al_T -O-Al) with a low chemical shift is formed (Fig. 5). As a result, the center of the peak for tetrahedrally coordinated Al is shifted towards a lower chemical shift.

3.2. Al-NMR after gas adsorption experiments

3.2.1. CO_2 and H_2O interaction with KMG30

1D ^{27}Al -NMR spectra recorded after exposing the pre-treated material to different sorbates are plotted in Fig. 6. During all experiments KMG30 was pre-treated with N_2 prior to the gas adsorption experiments. Therefore, the 1D-spectrum shown in Fig. 5 of pre-treated KMG30 can be used as a reference (red dotted line in Fig. 6a). It can be seen as that the spectrum after CO_2 adsorption shows only minor changes. The peak at 68 ppm for tetrahedrally

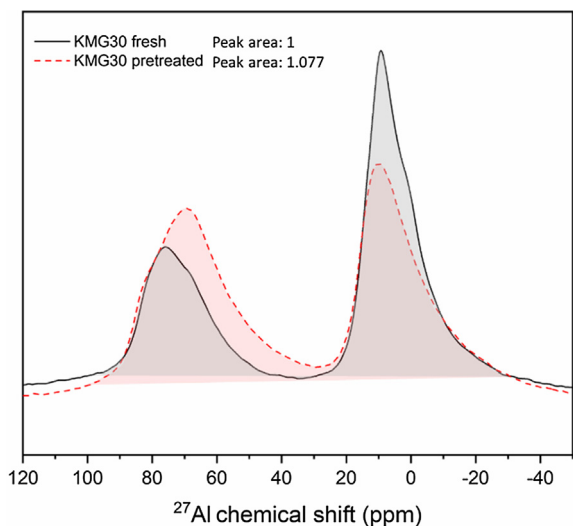


Fig. 5. Normalized ^{27}Al NMR spectra with respect to the sample weight before and after heat treatment.

coordinated Al decreased slightly and shows a shoulder at higher chemical shift (82 ppm). Comparison with the 2D spectrum of KMG30 after exposure to CO_2 to the pretreated material confirms that there are only minor changes in the Al coordination. This implies, that the irreversible amount of CO_2 remaining usually on the sorbent structure after exposure to CO_2 and regeneration with N_2 (Coenen et al., 2017, 2016; Ebner et al., 2006) is probably chemically bound to Mg^{2+} or K^+ or to non-coordinated Al centers, but not to well-coordinated Al that can be measured by NMR. In case the sorbent is exposed to H_2O (Fig. 6a), similar to the exposure to CO_2 , no significant changes are observed. It is confirmed in the literature, that CO_2 and H_2O adsorption and desorption usually does not affect the Al environment of calcined hydrotalcites at relatively low temperatures (30–80 °C) (Torres-Rodríguez et al., 2011). The present results show that this observation also holds for reversible CO_2 and H_2O adsorption at a much higher temperature (400 °C).

The binding energy of Mg, Al and K was measured with XPS for KMG30 after exposure to CO_2 , H_2O and H_2S and compared to the pre-treated sample (Table 3). For all three metals (Mg, Al and K), a slight increase in the binding energy was observed, after expo-

sure to CO_2 (EXP 2.1), which could be partially reversed when the materials were exposed to H_2O or H_2S after CO_2 (EXP 2.3 and further). Exposure to a mixture of both CO_2 and H_2O after CO_2 exposure did not strongly affect the binding energy. The small shift is most likely due to the replacement of a basic O ligand by formate or (bi)carbonate species at the surface. The trends suggest that these latter species decompose/desorb fastest from the Al sites, followed by Mg and K.

XPS was also used to semi-quantitatively follow the amount carbonate and sulfur species at the surface. The presence of carbonate-like species is evident from the C 1s feature at 288.8 eV. This signal is present in all samples, showing the strongly basic nature of the parent material from which, it is difficult to remove all carbonate species. Exposure to CO_2 leads to an increase in the amount of surface carbonate species. This signal does not change much if the sorbent is exposed to CO_2 and H_2O afterwards (EXP 2.2). This is contrary to the results obtained with TGA and PBR experiments, where it was found that the main part of adsorbed CO_2 is released by exposing the sorbent to H_2O at high operating temperatures (Coenen et al., 2018c, 2016). The reason can be that XPS probes also part of the bulk carbonate species, which cannot be decomposed under the applied conditions. For KMG30 only about 18 wt% of chemisorbed CO_2 would remain on the sorbent considering the capacity of the first breakthrough of CO_2 and a breakthrough after the sorbent was regenerated with steam ($T_{\text{exp}} = 400$ °C, $P_{\text{CO}_2} = 0.1$ bar, $P_{\text{H}_2\text{O}} = 0.025$ bar and 30 min regeneration with N_2 and 30 min regeneration with steam). However, when the sample was kept in H_2O only (without CO_2 , EXP 2.3) the carbonate signal decreased even below the value of the pre-treated material. This observation is in keeping with the TGA results. In fact we reported in an earlier study that a pre-treated sorbent still can release CO_2 if exposed to steam at 400 °C which is more apparent at higher temperature (Coenen et al., 2018a).

3.2.2. H_2S interaction with KMG30

The interaction of H_2S with the sorbent was investigated in the 5, 6 and 9 (Table 2). Fig. 6b shows that H_2S induces clear changes in the Al coordination of the mixed metal oxide structure. Two main observations can be made based on the Al-NMR spectra. First, the amount of visible octahedral Al increases upon H_2S adsorption. Second, the amount of tetrahedral Al is lowered, and an additional tetrahedral Al signal appears at 93 ppm with a small shoulder at 80 ppm. The appearance of the shoulder at 82 ppm is similar to

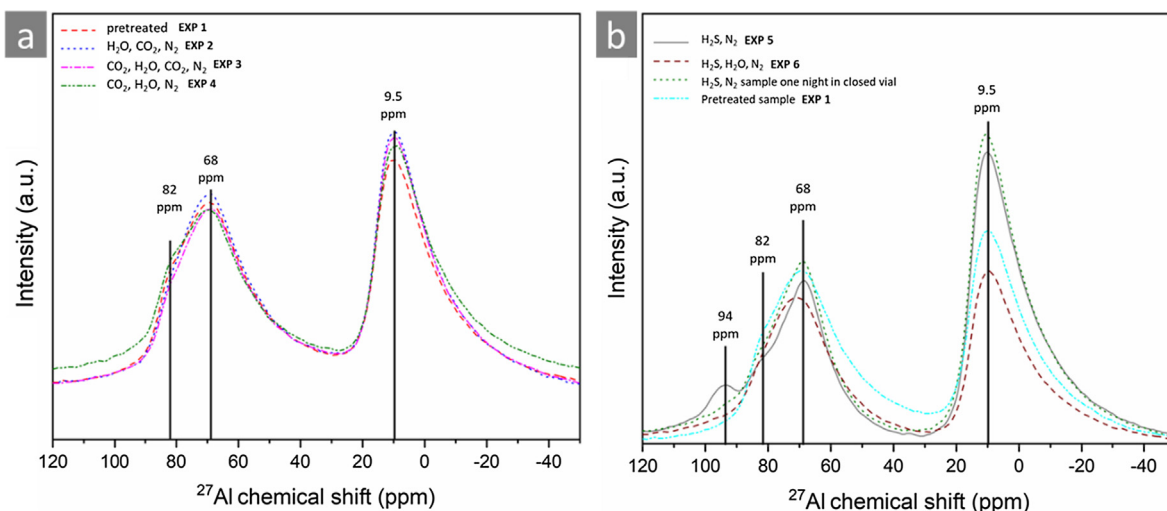


Fig. 6. 1D (a) ^{27}Al -NMR spectra (normalized with respect to sample mass) recorded for KMG30 after exposure to CO_2 and H_2O in different sequences; (b) ^{27}Al -NMR spectra (normalized with respect to sample mass) recorded for KMG30 exposed to H_2S , N_2 and H_2O in different sequences.

Table 3
X-Ray Photoelectron Spectroscopy analysis results of pretreated and treated sorbent material (KMG30).

EXP	Treatment	Binding energy Mg 1s (eV)	Binding energy Al 2p (eV)	Binding energy K 2p 3/2 (eV)	O–C=O/Al	S/Al
1	N ₂	1303.0	73.4	292.6	0.015	0
2	CO ₂ → N ₂	1303.5	73.9	293.0	0.025	0
3	CO ₂ → H ₂ O → N ₂	1303.4	73.6	292.9	0.028	0
4	H ₂ O → N ₂	1303.1	73.5	292.8	0.011	0
5	H ₂ S → N ₂	1303.1	73.6	292.7	0.021	0.058
6	H ₂ S → H ₂ O → N ₂	1303.0	73.4	292.6	0.013	0.015

what was obtained during the experiment with CO₂ (EXP 2). Assuming that the two peaks at 82 ppm and 68 ppm are due to the tetrahedral Al species in Al_T-O-Mg and Al_T-O-Al, the peak at 94 ppm should be caused by the interaction of Al with H₂S. The 2D spectrum (EXP 2.6, Fig. 6) clearly revealed a different site for tetrahedral Al after H₂S adsorption. A possible pathway could be the exchange of O by S in the structure resulting in (Al_T-S-Mg) and/or (Al_T-S-Al) tetrahedral complexes. The higher chemical shift observed is due to a higher electron density on the metal in the formed complex.

Exposure to H₂S leads to a significant increase in the amount of S species at the surface. From the binding energy at 161.5 eV, we infer that these species are predominantly sulfides (Fig. 3a). The formation of sulfides and the changes in tetrahedral Al can be reversed, when the sorbent is exposed to H₂O (see ²⁷Al-NMR 1D spectrum in Fig. 2b, and the ²⁷Al-2D spectrum in Fig. 7). This was also confirmed by XPS. The amount of sulfur species is decreased significantly upon H₂O exposure (EXP 2.5, Table 1). The chemical

shift observed for Al by XPS (Table 3) was slightly higher for Al compared to Mg and K when exposed to H₂S. This confirms, that Al is interacting with H₂S, which is partially reversible if the sorbent is exposed to steam afterwards. We have reported earlier, that H₂O exposure indeed leads to removal of adsorbed H₂S at elevated temperatures (Coenen et al., 2018b). It has been reported that H₂S can dissociatively adsorb on γ-Al₂O₃ leading to H₂O formation according to Eq. (1) (Datta and Cavell, 1985; Reshетенko et al., 2002; Wakker et al., 1993).



A more complex reaction mechanism was reported elsewhere, where the interaction of H₂S with mixed metal oxides was proposed with three different reactions on metal oxide (MO; Eqs. (2)–(4)) explaining the decomposition of formed sulfide complexes upon exposure to steam [14]:

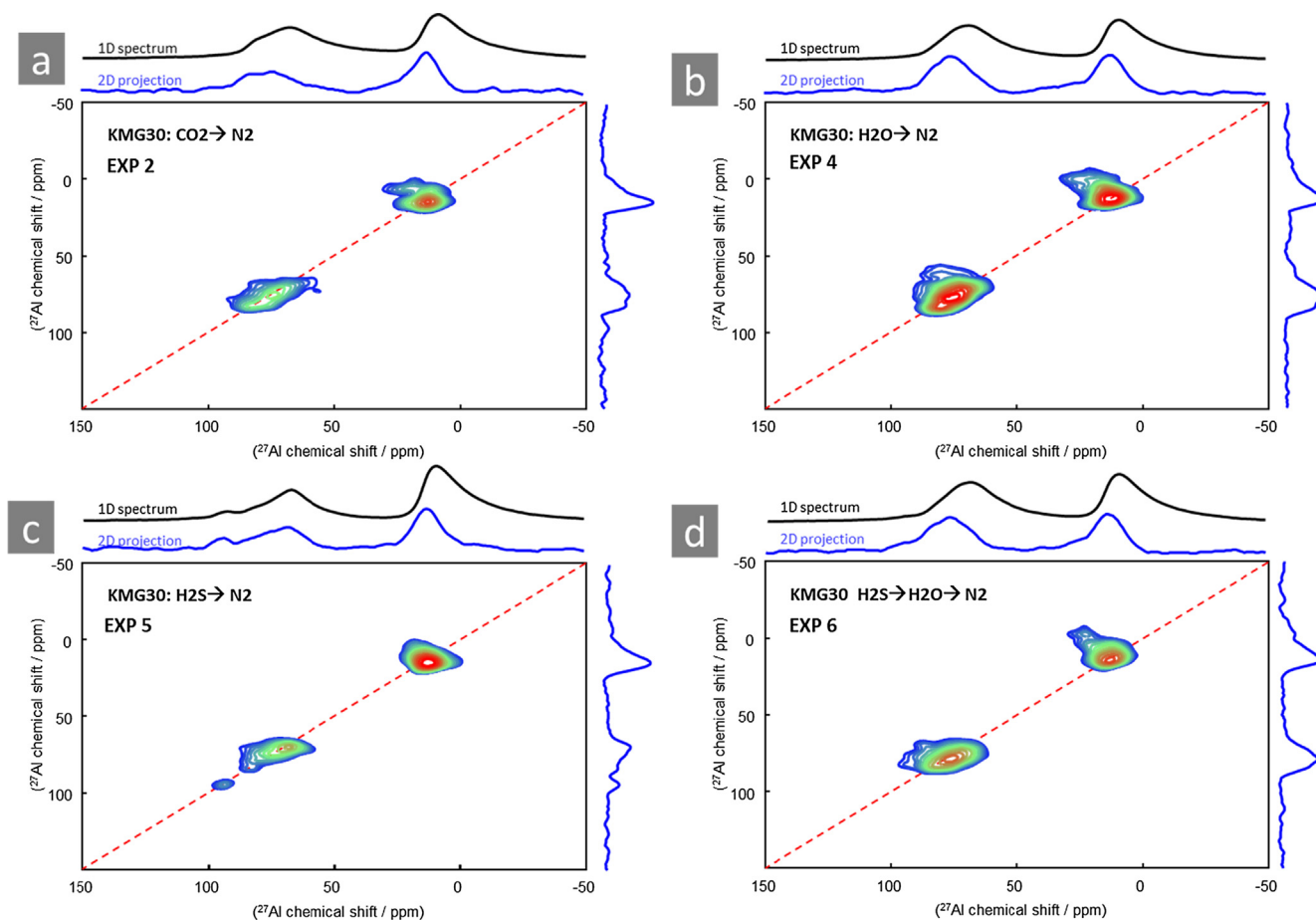


Fig. 7. 2D ²⁷Al-NMR spectra recorded of KMG30 after sorbate treatment at elevated temperature.

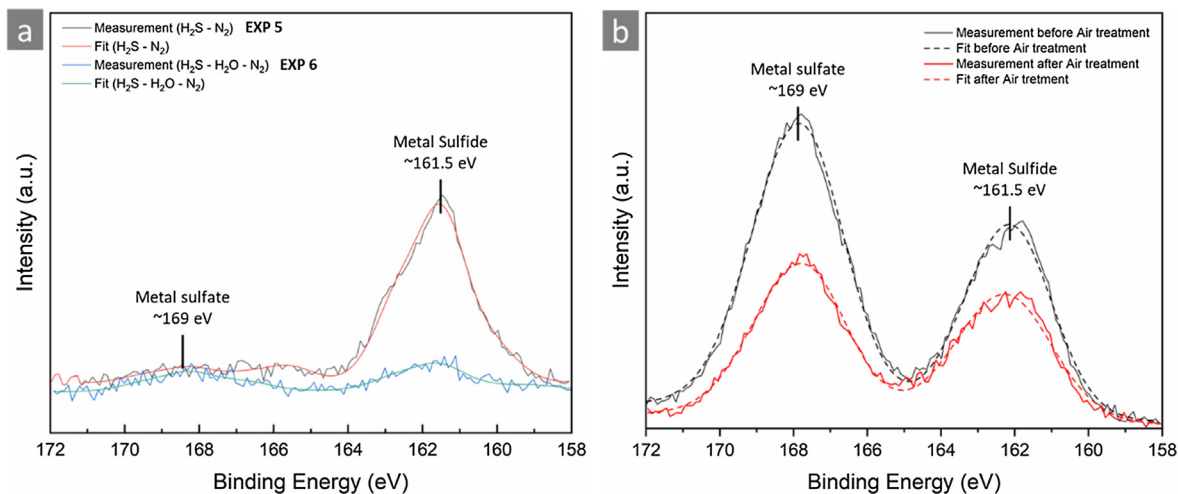


Fig. 8. (a) S 2p scan of sorbent exposed to H₂S and N₂ and H₂O in different sequence prepared under N₂ (b) S 2p scan of sorbent exposed to H₂S within a multicyle experiment at 400 °C after the experiment and after 8 h exposed to ambient conditions.



Decomposition of sulfur species formed on the sorbent takes place when the sorbent is exposed to ambient conditions. When the NMR rotor was kept for one night in a vial with air, the tetrahedral Al peak with a high chemical shift at 93 ppm disappeared, whereas the amount of octahedral Al remains constant. We also investigated a sorbent exposed to H₂S in multiple cycles. This sample showed a reversible change in color. When the sorbent material was exposed to ambient conditions for a long time, the yellow color disappeared together with a noticeable odor of H₂S. We conducted XPS measurements of a sorbent exposed to H₂S at 400 °C in a multicyle experiment as reported elsewhere (Coenen et al., 2018b). XPS spectra were recorded directly after the experiment and after an additional exposure to ambient for 8 h (laboratory conditions). Fig. 8b shows the resulting XPS S 2p spectra. In both cases, peaks corresponding to metal sulfide (~161.5 eV) and metal sulfate (~169 eV) were observed. After exposure to ambient conditions, the intensity of both peaks was significantly reduced. However, the quasi *in situ* experiments showed only a peak corresponding to metal sulfide. Therefore, exposure to ambient conditions leads to the oxidation of metal sulfide, resulting in the formation of metal sulfate, which will then react further to H₂S and be released. This is important regarding the regeneration of hydrotalcite-based adsorbents, which can be regenerated very efficiently with steam. Subsequent steam condensation can be used to obtain a H₂S-rich gas stream. In particular, these sorbents may be used in a gas sweetening process which could be competitive to the conventional amine-based gas sweetening process. The application of hydrotalcite-based sorbents for a gas sweetening process needs to be evaluated in the future.

4. Conclusions

A comprehensive study on the thermal behavior of different hydrotalcite materials and the interaction with different sorbates using ²⁷Al-NMR and XPS is presented in this study. It was found that Al coordination changes during a thermal treatment where octahedrally coordinated Al is transformed into tetrahedrally coordinated Al. 2D ²⁷Al-NMR showed that two different tetrahedrally coordinated sites are present, where the resonance with a higher chemical shift is attributed to the incorporation of Al in the Mg

matrix. Adsorption experiments with CO₂ and H₂O did not show any significant change in Al coordination, indicating that well-coordinated Al seems not to participate in the chemisorption mechanism at high temperatures. XPS revealed that upon CO₂ adsorption an increase in the binding energy was observed, which was partly reversible upon exposure to H₂O (with corresponding desorption of CO₂) indicating that different metals in the sorbent matrix are responsible for the reversible CO₂ chemisorption.

H₂S chemisorbs strongly on a hydrotalcite-based adsorbent. NMR revealed a clear interaction of coordinated Al with H₂S visible by additional tetrahedrally coordinated Al with a high chemical shift. Based on XPS analysis, it can be concluded that a metal sulfide is formed on the sorbent, which is reversible if the material is exposed to H₂O (both at high temperature and at room temperature). Decomposition of formed sulfide species involves the formation of sulfate species due to oxidation of sulfur and finally decomposition to H₂S. The results provide useful insights regarding the regeneration of hydrotalcite-based adsorbents for SEWGS or gas sweetening processes.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ces.2019.01.046>.

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