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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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Abstract

The role of aluminum in the structure of hydrotalcite-based sorbents was investigated with $^{27}$Al-NMR and XPS with respect to the chemisorption mechanism of different sorbate species, such as CO$_2$, H$_2$O and H$_2$S, 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 CO$_2$ and H$_2$O adsorption does not seem to influence well-coordinated Al, as observed with NMR, chemisorption of H$_2$S 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 H$_2$O.

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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 CO$_2$ and H$_2$S. The most common sorbents are based on hydrotalcites of MgO and Al$_2$O$_3$, which are usually impregnated with K$_2$CO$_3$ to increase the surface basicity. Usually the unit cell composition of the original Mg/Al hydrotalcite is described before calcination as [Mg$_6$Al$_2$(HO)$_{16}$CO$_3$]$^{2-}$ $\times$ 4 H$_2$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; Dragicic 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/Al$_2$O$_3$ 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...
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, $^{27}\text{Al}$-NMR and $^1\text{H}$ 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 CO$_2$ and H$_2$O 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 CO$_2$, H$_2$O and H$_2$S using both $^{27}\text{Al}$-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 H$_2$O, H$_2$S and CO$_2$. The focus was on finding the sorbent with the highest cyclic working capacity for CO$_2$, but also to understand the interaction of CO$_2$ with H$_2$O and H$_2$S in order to predict the sorption behavior for sorbates 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 H$_2$O during the adsorption of CO$_2$ has different effects: First, co-adsorption of CO$_2$ and H$_2$O 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, CO$_2$ and H$_2$O compete depending on their partial pressure, which could lead to a replacement of CO$_2$ by H$_2$O when the partial pressure of H$_2$O is increased (Coenen et al., 2017). This competition of CO$_2$ and H$_2$O results in an enhanced regeneration of the sorbent. The regeneration capacity of CO$_2$ can therefore be improved significantly by using steam instead of an inert such as N$_2$. In Fig. 1 we show the effect of regeneration on the breakthrough time (hence adsorption capacity for CO$_2$), which was determined with packed-bed reactor experiments using KMG30 as a sorbent with identical time (1 h) for regeneration. The breakthrough time for CO$_2$ is about twice as long, when the sorbent was regenerated with steam (red dotted line) compared to the regeneration with N$_2$ (red line), and consequently more CO$_2$ 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.

To describe the adsorption behavior of a binary mixture such as combination of CO$_2$ and H$_2$O, or H$_2$S and H$_2$O, a phenomenological model was developed considering different adsorption sites. Weaker bond sorbate can be easily regenerated with N$_2$, 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 CO$_2$ which can be regenerated with N$_2$ compared to the other sorbents. Sorbent material with a high Al$_2$O$_3$ content (such as KSORB, Table 1) show a higher cyclic working capacity for the exchange site (e.g. CO$_2$ replacing H$_2$O and vice versa) (Coenen et al., 2018c). From this observation one may conclude that Al$_2$O$_3$ in combination with K$_2$CO$_3$ 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. N$_2$). KMG30 showed the highest cyclic working capacity for CO$_2$ 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 H$_2$S 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 CO$_2$, H$_2$O and H$_2$S with semi in situ NMR and XPS which will be discussed in this publication.

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**Nomenclature**

| Symbol | Definition |
|--------|------------|
| Al$_T$ | tetrahedrally coordinated aluminum |
| Al$_O$ | octahedrally coordinated aluminum |
| HTC    | hydrotalcite based material |
| TGA    | thermogravimetric analysis |

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1. For interpretation of color in Figs. 1 and 6, the reader is referred to the web version of this article.
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-calcinated 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 H2O and CO2 (Coenen et al., 2016). 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.

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

| Material | Mg/Al | Al/K | Mg/K | K2CO3 wt% |
|----------|-------|------|------|-----------|
| KSORB    | –     | 5.42 | –    | 20        |
| KMG30    | 0.54  | 3.79 | 2.06 | 20        |
| KMG70    | 2.95  | 1.63 | 4.80 | 20        |

Table 2 Overview of the different semi-in situ experiments and the used characterization techniques on KMG30 treated with different gases (P_{CO2} = 0.66 bar, P_{H2S} = 0.34 bar, P_{H2O} = 0.03 bar, temperature was 400 °C during the treatment; step duration was 30 min for each reaction step).

| Exp. number | Treatment | XPS | 27Al-NMR |
|-------------|-----------|-----|----------|
| 1           | Pretreatment with N2 | X | X |
| 2           | CO2 → N2 | X | X |
| 3           | CO2 → H2O → N2 | X | X |
| 4           | H2O → N2 | X | X |
| 5           | H2S → N2 | X | X |
| 6           | H2S → H2O → N2 | X | X |
| 7           | H2O → CO2 → N2 | X | X |
| 8           | H2O → CO2 → H2O → N2 | X | X |
| 9           | H2S → N2 (hydrated in air) | X | X |

Fig. 2. Small test reactor for sample treatment under reactive atmosphere.
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 octahedral Al species in the original hydrotalcite 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.]
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 γ-Al2O3 but the AlT/AlO 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 AlT are different for different Al/Mg ratios and are generally higher than for the K2CO3 promoted Al2O3, but also higher than for unpromoted Al2O3 (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 mentioned study were not impregnated with K2CO3. 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 KGM30 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 (AlT–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. CO2 and H2O interaction with KGM30

1D 27Al-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 N2 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 CO2 adsorption shows only minor changes. The peak at 68 ppm for tetrahedrally
coordinated Al decreased slightly and shows a shoulder at higher chemical shift (82 ppm). Comparison with the 2D spectrum of KMG30 after exposure to CO₂ to the pretreated material confirms that there are only minor changes in the Al coordination. This implies, that the irreversible amount of CO₂ remaining usually on the sorbent structure after exposure to CO₂ and regeneration with N₂ (Coenen et al., 2017, 2016; Ebner et al., 2006) is probably chemically bound to Mg²⁺ 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 H₂O (Fig. 6a), similar to the exposure to CO₂, no significant changes are observed. It is confirmed in the literature, that CO₂ and H₂O 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 CO₂ and H₂O 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 CO₂, H₂O and H₂S 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 exposure to CO₂ (EXP 2.1), which could be partially reversed when the materials were exposed to H₂O or H₂S after CO₂ (EXP 2.3 and further). Exposure to a mixture of both CO₂ and H₂O after CO₂ 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 CO₂ leads to an increase in the amount of surface carbonate species. This signal does not change much if the sorbent is exposed to CO₂ and H₂O 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 CO₂ is released by exposing the sorbent to H₂O 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 CO₂ would remain on the sorbent considering the capacity of the first breakthrough of CO₂ and a breakthrough after the sorbent was regenerated with steam (Texp = 400 °C, PCO₂ = 0.1 bar, PH₂O = 0.025 bar and 30 min regeneration with N₂ and 30 min regeneration with steam). However, when the sample was kept in H₂O only (without CO₂, 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 CO₂ if exposed to steam at 400 °C which is more apparent at higher temperature (Coenen et al., 2018a).

3.2.2. H₂S interaction with KGM30

The interaction of H₂S with the sorbent was investigated in the 5, 6 and 9 (Table 2). Fig. 6b shows that H₂S induces clear changes in the Al coordination of the mixed metal oxide structure. Two main observations can be made based on the 27Al-NMR spectra. First, the amount of visible octahedral Al increases upon H₂S 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
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 Al₇-O-Mg and Al₇-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 (Al₇-S-Mg) and/or (Al₇-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; Reshetenko et al., 2002; Wakker et al., 1993).

\[ H_2S + [O] \rightarrow H_2O + [S] \]  

(1)

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]:

\[ H_2S + MO \rightarrow MS + H_2O \]  

(2)

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

| EXP | Treatment | Binding energy | Binding energy | Binding energy | O=C=O/Al | S/Al |
|-----|-----------|----------------|----------------|----------------|----------|------|
|     |           | Mg 1s (eV)     | Al 2p (eV)     | K 2p 3/2 (eV)  |          |      |
| 1   | N₂        | 1303.0         | 73.4           | 292.6          | 0.015    | 0    |
| 2   | CO₂ → N₂ | 1303.5         | 73.9           | 293.0          | 0.025    | 0    |
| 3   | CO₂ → H₂O → N₂ | 1303.4       | 73.6           | 292.9          | 0.028    | 0    |
| 4   | H₂O → N₂ | 1303.1         | 73.5           | 292.8          | 0.011    | 0    |
| 5   | H₂S → N₂ | 1303.1         | 73.6           | 292.7          | 0.021    | 0.058|
| 6   | H₂S → H₂O → N₂ | 1303.0       | 73.4           | 292.6          | 0.013    | 0.015|

Fig. 7. 2D ²⁷Al-NMR spectra recorded of KMG30 after sorbate treatment at elevated temperature.
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 H$_2$S 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 H$_2$S. We conducted XPS measurements of a sorbent exposed to H$_2$S at 400 °C in a multicycle 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 H$_2$S and be released. This is important regarding the regeneration of metal sulfide species due to oxidation of sulfur and finally decomposition to H$_2$S. 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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