The Catalytic Mechanism of Intercalated Chlorine Anions as Active Basic Sites in MgAl-layered Double Hydroxide for COS Hydrolysis

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Abstract

In order to make clear the role of intercalated anions in layered double hydroxides (LDHs) for catalytic hydrolysis of COS, the adsorption and reaction characteristics of COS over the simple $\text{Mg}_2\text{Al-Cl-LDH}$ model catalyst were studied by both theoretical and experimental methods. Density functional theory (DFT) calculations by CASTEP found that the chloride ions in LDH function as the key Brønsted-base sites to activate the adsorbed H_2O with enlarged bond length and angle, facilitate the dissociative adsorption of intermediates including mono-thiocarbonic acid (MTA) and hydrogen thiocarbonic acid (HTA), and participate in the formation of transient states and subsequent hydrogen transfer process with decreased energy barriers during COS hydrolysis. COS hydrolysis will preferentially go through the dissociated intermediates of mono-thiocarbonates (MT) and hydrogen thiocarbonates (HT) with dramatically decreased energy barriers, and the rate-determining step of COS hydrolysis over $\text{Mg}_2\text{Al-Cl-LDH}$ will be the nucleophilic addition of C=O in COS by H_2O ($E_a = 1.10$ eV). The experimental results further revealed that the apparent activation energy (0.89 eV) of COS hydrolysis over $\text{Mg}_2\text{Al-Cl-LDH}$ is close to theoretical value (1.10 eV), and the accumulated intermediates of MT, HT or carbonate were also observed by FT-IR around 1363 cm^{-1} on the used $\text{Mg}_2\text{Al-Cl-LDH}$, which are well in accordance with the theoretical prediction. The demonstrated participation of intercalated chlorine anions in the evolution of intermediates and transient states as Brønsted-base sites during COS hydrolysis will give new insight into the basic sites in LDH materials.

Introduction

Layered double hydroxides (LDHs) are a class of layered host-guest 2D materials, which have been considered as excellent solid base catalysts for many catalytic reactions such as aldol reaction, knoevenagel condensation, michael additions, transesterification reaction (Bing et al. 2018; Liu et al. 2014; Wang et al. 2011; Winter et al. 2006). The general formula of LDHs can be denoted as $[\text{M}^{2+}_{1-x}\text{M}^{3+}_x(\text{OH})_2]^{x+}(\text{A}^{n-}_{x/n}) \cdot m\text{H}_2\text{O}$, where M^{2+} and M^{3+} are metal cations such as Mg^{2+} , Ni^{2+} , Mn^{2+} , Zn^{2+} , or Al^{3+} , Ga^{3+} , Fe^{3+} , Cr^{3+} occupying octahedral positions in hydroxide layers; x is the molar ratio of the trivalent cation $\text{M}^{3+}/(\text{M}^{2+}+\text{M}^{3+})$, and A denotes interlayer charge-compensating anions (Benhiti et al. 2020; Chaillot et al. 2020; Yan et al. 2010). Traditionally, the hydroxyl groups in LDHs were regarded as the active basic sites participating in catalytic reaction (Rao et al. 1998; Winter et al. 2005). However, Moraes et al. (2016), Costa et al. (2012) and Liu et al. (2020) have recently revealed that the most basic sites in LDHs are the interlayer anions (PO_4^{3-} , CO_3^{2-} , Cl^-) rather than hydroxyl group in the layer through the structural analysis by Density functional theory (DFT). Therefore, how the intercalated anions function as the basic sites is still an unclear issue in these specific base-catalyzed reactions over LDH materials.

Carbonyl sulfide (COS) is one of the main malodorous and toxic organic sulfur compounds in industrial gases, which may poison the catalysts as well as cause serious environmental pollution (Cheng et al. 2015; Harnisch et al. 1995; Labaki and Jeguirim 2017; Yao et al. 2015). The removal of COS through catalytic hydrolysis over the solid base catalysts is one of the most effective strategy with the

advantages of high efficiency, low operation cost, and mild reaction condition in industry (Chiche and Schweitzer 2017; Li et al. 2020; Zhao et al. 2020). As the typical solid base catalyst, LDHs and its calcined mixed metal oxides (MMO) exhibit excellent catalytic activity for COS hydrolysis as reported by Wang et al. (2012), Zhao et al. (2013b) and Song et al. (2019). Recently, Mi et al. (2019) demonstrated the excellent activity and stability for COS hydrolysis over the mechanochemically synthesized MgAl-LDHs with intercalated CO_3^{2-} , and their outstanding performances were attributed to the abundant hydroxyl groups in LDHs. On the other hand, the study by Ryzhikov et al. (2011) about the activated LDHs containing CO_3^{2-} implied that the CO_3^{2-} ions at external surface may be the active sites for COS hydrolysis. Until now, the exact type of key basic sites in LDHs and their catalytic mechanism have remained largely unknown for COS hydrolysis.

It is generally believed that COS hydrolysis obeys the addition mechanism through the intermediates of the mono-thiocarbonic acid (MTA) and hydrogen thiocarbonic acid (HTA) (See their detailed structure in Fig. S1) (Guo et al. 2016; Svoronos and Bruno 2002). Recently, Song et al. (2017), Ning et al. (2017) and Song et al. (2019) have done well work to explore the catalytic reaction mechanism of COS hydrolysis over different oxide catalysts such as Fe_2O_3 , CeO_2 , MgAlCe by DFT, and the undissociated MTA and HTA were considered as intermediates during the catalytic hydrolysis of COS. However, many experiment results by infrared spectrometer indicated the existence of the dissociated intermediates of mono-thiocarbonates (MT) or hydrogen thiocarbonates (HT) during COS hydrolysis over the oxide catalysts (Aboulayt et al. 1996; Liu et al. 2007; Toops and Crocker 2008; Zhao et al. 2020). In addition, early research by George (1974) also proposed the hydroxyl involved nucleophilic addition mechanism through the dissociated intermediates of MT over alumina. Thus, the reaction path of COS hydrolysis through these dissociated intermediates of MT/HT is also possible and should be considered over the basic sites in LDHs.

In this work, the simple chlorine intercalated $\text{Mg}_2\text{Al-Cl-LDH}$ is chosen and prepared as the model catalyst to identify the active basic sites and make clear their catalytic mechanism for COS hydrolysis over LDH materials. The different adsorption configurations of reactants, intermediates and products were explored by DFT to make sure their best adsorption sites and most likely existence forms on $\text{Mg}_2\text{Al-Cl-LDH}$ surface. Moreover, the reaction pathways through both the undissociated and dissociated intermediates were considered, and the corresponding transient states and activation energies were calculated to find out the most possible reaction channels and rate-determining step for COS hydrolysis over the chlorine intercalated LDH material. In addition, the $\text{Mg}_2\text{Al-Cl-LDH}$ were prepared by coprecipitation method to evaluate its catalytic performance and apparent activation energy, and the accumulated reaction intermediates in the used $\text{Mg}_2\text{Al-Cl-LDH}$ were also detected by infrared spectroscopy. The results of this work reveal that the chlorine ions in $\text{Mg}_2\text{Al-Cl-LDH}$ act as the crucial basic sites to activate H_2O molecule and participate in the evolution of intermediates and transient states during COS hydrolysis, which will give new insight into the basic sites in LDHs materials.

1. Method

1.1. Computational Model

The computational model of $\text{Mg}_2\text{Al-Cl-LDH}$ was constructed according to the previous report by Yan et al. (2010). The 2H-polytyped model was chosen using the atomic coordinates of naturally occurring sjögrenite with the unit cell parameters: $a = b = 0.3100$ nm, $c = 1.560$ nm, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$, $P6_3/mmc$ space group (Taylor 1973). In geometry optimization of the compounds, all atoms and unit cell parameters were relaxed. The final model of $\text{Mg}_2\text{Al-Cl-LDH}$ was obtained as shown in Fig. 1A-B, and the calculated cell parameters for these compounds are summarized in Table S1. As the preferentially exposed crystal face, the (0 0 3) face of $\text{Mg}_2\text{Al-Cl-LDH}$ was cut with $p(2 \times 2 \times 1)$ supercells, and the vacuum region between slabs is 20 Å. Before the adsorption and reaction of COS, all the atoms in the cut cell were relaxed as shown in Fig. 1B1-B2.

1.2. Computational Method

The first-principle DFT calculations were performed with the plane wave method in Cambridge Sequential Total Energy Package (CASTEP) (Segall et al. 2002). The Perdew-Burke-Ernzerhof (PBE) in generalized gradient approximation (GGA) was used as the exchange-correlation functional (Payne et al. 1992; Perdew et al. 1996). The Tkatchenko Scheffler method was used for the DFT dispersion correction to deal with the hydrogen bonding and van der Waals interactions in LDHs (Tkatchenko and Scheffler 2009). The ionic cores are described by ultrasoft pseudopotentials, and the BFGS algorithm was used to search the potential energy surface during optimization (Anglada and Bofill 1998; Bajdich et al. 2013; García-Mota et al. 2012; Valdés et al. 2008). The calculation parameters are with the energy tolerance of 1×10^{-5} eV per atom, a maximum force tolerance of 0.03 eV/Å, and a maximum displacement tolerance of 1×10^{-3} Å. The k-point meshes used for the Brillouin zone integrations are $3 \times 3 \times 1$, and a Fermi smearing of 0.1 eV and the cut-off energy of 340 eV are used according to the results by Liu et al. (2020). Before geometry optimization of molecules, a periodic cube cell with the side length of 20 Å was built. The molecular geometries of the reactants, transition states (TS), intermediate complexes (IM), and products were calculated and optimized using the same method and parameters as above by DFT. The TS Search with the complete Linear synchronous transit/Quadratic synchronous transit (LST/QST) method was used to find the transition states connect to the intended reactants and products, and the TS Confirmation were executed to confirm the found transition states. The adsorption energy (E_{abs}) was defined as Eq. 1. $E_{adsorbate/catalyst}$ is the total energy of the adsorbate/catalyst system after the gas molecule being adsorbed on model catalyst. $E_{adsorbate}$ is the energy of gas molecule and $E_{catalyst}$ is the energy of the model catalyst after geometry optimization.

$$E_{abs} = E_{adsorbate/catalyst} - E_{adsorbate} - E_{catalyst} \quad (1)$$

1.3. Experimental Method

All inorganic chemical compounds (e.g., NaOH, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$) were purchased from Macklin (Shanghai) without further purification. To avoid the introduction of CO_3^{2-} in LDHs, the deionized

water was boiled before use in all the experimental processes. $\text{Mg}_2\text{Al}-\text{Cl}-\text{LDH}$ was synthesized by the co-precipitation method (Jaymand 2011). Typically, solution A was obtained by dissolving 0.16 M $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and 0.08 M $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ in 200 mL deionized water. Solution B contained 1 M NaOH in 200 mL deionized water. Then, solution B was added dropwise to solution A under vigorous stirring at room temperature, and the resulting suspension was stirred at 60 °C for 2 h. Subsequently, the suspension was transferred to a sealed Teflon aging at 105 °C for 12 h. The precipitate was filtered out, washed several times with deionized water until filtrate is neutral, and dried at 100 °C for 12 h to obtain the $\text{Mg}_2\text{Al}-\text{Cl}-\text{LDH}$.

The crystal structure of the as-synthesized $\text{Mg}_2\text{Al}-\text{Cl}-\text{LDH}$ was confirmed by an X-ray diffraction analyzer (XRD, Smartlab) with a scanning rate of 0.02 °/s in 5–90 ° for 2θ at 40 kV and 200 mA. The scanning electron microscope (SEM, JSM-7800prime) with an accelerating voltage of 15 kV was used to observe the morphology of $\text{Mg}_2\text{Al}-\text{Cl}-\text{LDH}$. The accumulated intermediate species in the used $\text{Mg}_2\text{Al}-\text{Cl}-\text{LDH}$ after COS hydrolysis were detected by the fourier transform infrared spectrometer (FT-IR, Tensor27, Bruker).

The catalytic performance of COS hydrolysis over $\text{Mg}_2\text{Al}-\text{Cl}-\text{LDH}$ was evaluated in the fixed bed reactor (10 mm in inner diameter) at atmospheric pressure using 0.5 g of catalyst (20 – 40 mesh). The total gas hourly space velocity is 4500 h^{-1} with 500 ppm COS, and the H_2O was injected into the reactor from a thermostatic water at 25 °C with the water vapor content of 2.9%. The concentration of COS was continually monitored on line by a gas chromatograph (SP-3420A) equipped with a flame photometric detector (FPD). The COS conversion was calculated as Eq. 2. The Arrhenius plots of COS hydrolysis over $\text{Mg}_2\text{Al}-\text{Cl}-\text{LDH}$ were obtained according to the data of COS conversion below 20% with the minimized effect of diffusion.

$$\text{COS conversion (\%)} = (\text{COS}_{\text{inlet}} - \text{COS}_{\text{outlet}}) / \text{COS}_{\text{inlet}} \times 100\% \quad (2)$$

2. Results And Discussion

2.1. The adsorption configurations of reactants

The adsorption is the first step for catalytic reaction, and the optimal adsorption configuration of $\text{H}_2\text{O}/\text{COS}$ will help to identify the active basic sites in LDHs. The adsorption of H_2O , COS as well as $\text{H}_2\text{O}/\text{COS}$ at the different sites on the (0 0 3) face of $\text{Mg}_2\text{Al}-\text{Cl}-\text{LDH}$ were explored as shown in Fig. 2, respectively. After geometry optimization of adsorbed H_2O at Mg site, Al site and Mg-Al bridge site (top view in Fig. 2A1-A3, side view in Fig. S2A1-A3), the two hydrogen atoms in H_2O are drawn by the nearby chloride ion pair and are nearly in the same plane with chloride ions. At the same time, the oxygen in H_2O interacts with the neighboring hydrogens in hydroxy groups of LDH through hydrogen bond (Hou et al. 2017; Nobeli et al. 2001). It is worth noting that the chloride ion pair significantly changes the structural parameter of H_2O with longer bond distance of O-H ($L_{\text{O-H}}$) and larger bond angle of H-O-H ($\theta_{\text{H-O-H}}$). Especially over the Mg-Al bridge sites (Fig. 2A3), the interaction between the Cl and H in H_2O is the strongest with the shortest distance of 2.08 Å. Correspondingly, the $L_{\text{O-H}}$ and $\theta_{\text{H-O-H}}$ are enlarged by the

chloride ion pair from 0.98 Å and 104.6° in gaseous H₂O to 1.00 Å and 110.9° in adsorbed H₂O, respectively. Moreover, the adsorption of H₂O over Mg-Al bridge site possesses the lowest adsorption energy (-0.78 eV, Fig. 1A3). The enlarged L_{O-H}/θ_{H-O-H} as well as the strong adsorption of H₂O will weaken the O-H bond in H₂O and facilitate its hydrolysis reaction with COS. These results clearly demonstrate the chloride ions in LDH can strongly interact with H atoms in adsorbed H₂O molecule, enlarge the L_{O-H} and θ_{H-O-H} in H₂O, and thus dramatically activate the H₂O for COS hydrolysis, which acts as the active sites for adsorption of H₂O in Mg₂Al-Cl LDH.

The adsorption of COS over the Mg site, Al site and OH site on LDH was shown in Fig. 2B1-B3 (top view) and Fig. S2B1-B3 (side view). It can be found that the oxygen in COS is also drawn by neighboring hydrogen of hydroxy groups in LDH, but the repulsive force between the S atom in COS and chlorine ion in LDH make the nearby chlorine ion away from its original location. The structural parameters of adsorbed COS change little and the adsorption energies are in the range from -0.27 eV to -0.19 eV, which are much smaller than that of the adsorbed H₂O. These results indicate the COS molecule weakly adsorbs on the LDH surface in comparison with H₂O.

The above results show the H₂O can adsorb much stronger than COS over LDH surface, and H₂O molecule will first occupy the optimal Mg-Al bridge site with the lowest adsorption energy. Figure 2C1-C3 shows the coadsorption of COS around the pre-adsorbed H₂O. Compared with the adsorption of the single H₂O or COS, both the H₂O and COS are away from their original positions, indicating the repulsive force exists between the adsorbed H₂O and COS. The coadsorption energy of the three configurations are all lower than that of adsorbed H₂O in Fig. 2B1-B3, and the coadsorption of COS at the OH site possesses the lowest adsorption energy of -0.86 eV. Another possible coadsorption model is the absorption of COS upon the adsorbed H₂O as shown in Fig. S3, which is similar with the coadsorption of H₂O/COS on the CeO₂(110) surface reported by Song et al. (2017). It can be found that the adsorption energy (-0.69 eV) is even higher than that for the adsorption of the single H₂O at the Mg-Al bridge site (-0.78 eV, Fig. 2A3), which indicates the adsorption model of COS upon the adsorbed H₂O will not be preferential. These results manifest both H₂O and COS will preferentially coadsorb at the surface sites on Mg₂Al-Cl-LDH, and the further hydrolysis reaction at low temperature (30–250 °C) will follow the Langmuir-Hinshelwood reaction mechanism (Chiche and Schweitzer 2017; Rhodes et al. 2000; Svoronos and Bruno 2002).

The successful occurrence of a chemical reaction needs proper orientation and energy according to the collision theory of chemical reaction. Although the coadsorption energies of H₂O/COS are close, the geometrical configurations for the coadsorption of COS at Mg or Al sites (Fig. 2C1-C2) are against the formation of conjugated structure during the nucleophilic addition of the C=O or C=S. Thus, the coadsorption of COS at OH site (Fig. 2C3) will be adopted as the optimal adsorption configuration (denoted as IM1) for COS hydrolysis.

Figure2 The geometrically optimized configurations of H₂O (A1-A3), COS (B1-B3) and H₂O/COS (C1-C3) adsorbed at the different sites on (0 0 3) face of Mg₂Al-Cl-LDH from top view with their adsorption energy labeled. (Atomic legend: -Cl, -C, -S, -H, -O, -Al, -Mg.)

2.2. The adsorption configurations of the possible intermediates

The MTA and HTA are the main possible intermediates during COS hydrolysis as displayed by many reports (See their detailed structure in Fig. S1) (Deng et al. 2007; Guo et al. 2016). The possible adsorption configurations of these intermediates over the surface of Mg₂Al-Cl-LDH will be explored in this part. Fig. S4 and Fig. 3 show the possible configurations of MTA adsorbed on the LDH surface. When the MTA was put parallelly up the LDH surface (Fig. S4A), the two H atoms of hydroxyl groups in MTA are drawn toward the neighbouring chlorine ion pair with the adsorption energy of -1.02 eV, indicating the strong interaction between the H atoms in MTA and the Cl ions in LDH. After putting the MTA close to the chlorine ion pair vertically (Fig. S4B), the interaction between the two H atoms of hydroxyl groups in MTA and the nearby chlorine ion pair increases significantly with much lower adsorption energy of -1.23 eV. The adsorption energy can further decrease to -1.42 eV if the MTA molecule is in the same plane with the chloride ions (Fig. S4C and Fig. 3A). It can also be seen from Fig. S4C that the S and O atoms in MTA can also interact with the nearby H atoms of surface hydroxyl in LDH with the bond length of 2.29 Å and 1.69 Å, respectively, which accounts for its decreased adsorption energy. Especially, the distance between H atoms in MTA and nearby Cl even achieves to 1.59 Å together with the enlarged O-H bond length in MTA from 0.99 Å (original state) to 1.19 Å (adsorbed state, Fig. 3A). The weakened O-H in MTA by Cl will make the hydrogen transfer in MTA easy during hydrolytic process. According to the above different adsorption configurations and their adsorption energies, MTA will preferentially adopt the lied adsorption configuration as shown in Fig. 3A.

Figure3 The different geometrical configurations of MTA (A) and its two dissociative adsorption products of MT~HCl (B, C) on the (0 0 3) face of Mg₂Al-Cl-LDH from top view together with their adsorption energies labeled. IM2a~IM2c are the serial numbers of the possible intermediates during COS hydrolysis, which are labeled at the bottom right of each adsorption configuration. (Atomic legend: -Cl, -C, -S, -H, -O, -Al, -Mg.)

Considering the dissociative adsorption of MTA to form MT as observed by the experimental results of FT-IR (Liu et al. 2007; Rhodes et al. 2000; Zhao et al. 2020), the possible adsorption configurations of MT over Mg₂Al-Cl-LDH are also explored. Fortunately, two possible adsorption configurations of MT (denoted as IM2b and IM2c) were found as shown in Fig. 3B-C by putting one of the hydroxyls in MTA much closer to Cl ion in LDH. Under the interaction of nearby chloride ion, any of the two hydrogen atoms in MTA can be dissociated to form adsorbed MT anion and hydrogen chloride (HCl), which clearly manifests the Cl ions in LDHs function as the Brønsted-base sites to interact with the acidic MTA. Moreover, the bond length of the adsorbed HCl (1.36 ~ 1.38 Å) is much longer than that of gaseous HCl (1.27 Å), implying the easy

hydrogen transfer between MTA and $\text{MT} \sim \text{HCl}$. To confirm this point, the transient state and activation energy of the hydrogen transfer between MTA and $\text{MT} \sim \text{HCl}$ was calculated as shown in Fig. S5, and the corresponding imaginary frequency of the transition state is shown in Table S2. The activation energies from MTA to $\text{MT} \sim \text{HCl}$ and from $\text{MT} \sim \text{HCl}$ to MTA are 0.05 eV and 0.10 eV, respectively. The very small activation energies of both forward reaction and reverse reaction verify the easy hydrogen transfer as well as the dissociation equilibrium between adsorbed MTA and $\text{MT} \sim \text{HCl}$ on LDH. Therefore, the $\text{MT} \sim \text{HCl}$ can also be the intermediates during COS hydrolysis over $\text{Mg}_2\text{Al-Cl-LDH}$.

The possible adsorption configurations of other intermediates during COS hydrolysis over $\text{Mg}_2\text{Al-Cl-LDH}$ are shown in Fig. 4. The different configurations of HTA and their dissociated $\text{HT} \sim \text{HCl}$ can all be found over the LDH surface from Fig. 4A1 to Fig. 4B3. Similar with the dissociative adsorption of MTA, the Cl ions in LDHs also function as the Brønsted-base sites to take in the H atom from HTA. Moreover, the adsorption energies of the dissociated $\text{HT} \sim \text{HCl}$ (-0.99 eV $\sim$ -0.75 eV) are observably lower than that of undissociated HTA (-0.75 $\sim$ -0.69). The lower adsorption energies indicate that the dissociated $\text{HT} \sim \text{HCl}$ is more stable and will be the dominant species over LDH surface, which are well consistent with the experimental results (Liu et al. 2007; Rhodes et al. 2000). The transient states and activation energies of the hydrogen transfer between HTA and $\text{HTA} \sim \text{HCl}$ were also calculated as shown in Fig. S6. Their activation energies of both forward reaction and reverse reaction are also small from 0.08 eV and 0.47 eV, implying the easy hydrogen transfer as well as the dissociation equilibrium between adsorbed HTA and $\text{HA} \sim \text{HCl}$ on LDH. In addition, the final hydrolysis products (H_2S and CO_2) adsorbed on $\text{Mg}_2\text{Al-Cl-LDH}$ are also shown in Fig. 4C, and its much higher adsorption energy of -0.17 eV indicates their easy desorption from the LDH surface, which is also supported by the experimental results by Fiedorow et al. (1984).

In brief, the MTA and HTA can strongly adsorbed in the same plane within the chloride ions on the LDH surface with the adsorption energies from 0.69 eV to 1.49 eV. The MTA and HTA are inclined to dissociate and exist in the form of dissociated $\text{MT} \sim \text{HCl}$ and $\text{HT} \sim \text{HCl}$ with much lower adsorption energies on LDH, and the Cl ions in LDHs function as the Brønsted-base sites to take in the H atoms from MTA or HTA. The low energy barriers are from 0.05 eV to 0.47 eV between MTA/HTA and their dissociated $\text{MT}/\text{HT} \sim \text{HCl}$ on LDH, implying the existence of dissociation equilibrium for MTA and HTA adsorbed on LDH.

Figure4 The different geometrical configurations of HTA (A1, B1), their possible dissociative adsorption products of $\text{HT} \sim \text{HCl}$ (A2, B2, B3), and the final hydrolysis products (H_2S and CO_2) adsorbed on the (0 0 3) face of $\text{Mg}_2\text{Al-Cl-LDH}$ from top view together with their adsorption energies labeled. IM3a $\sim$ IM5 are the serial numbers of the possible intermediates during COS hydrolysis, which are labeled at the bottom right of each adsorption configuration. (Atomic legend: -Cl, -C, -S, -H, -O, -Al, -Mg.)

2.3. The possible reaction channels

Considering the existence of the dissociation equilibrium of MTA and HTA on LDH with small energy barriers (< 0.5 eV), the role of the dissociated $\text{MT} \sim \text{HCl}$ and $\text{HT} \sim \text{HCl}$ should be considered in the reaction mechanism of COS hydrolysis over $\text{Mg}_2\text{Al-Cl-LDH}$. This part will find out and compare the transition

states and activation energies through/non-through the dissociated MT ~ HCl and HT ~ HCl to find the most possible reaction pathways for COS hydrolysis.

Figure 5 shows the transient states and activation energies through the dissociated MT ~ HCl and HT ~ HCl for COS hydrolysis over the (0 0 3) face of Mg₂Al-Cl-LDH together with their imaginary frequencies listed in Table S2. Normally, the first step for COS hydrolysis will be through the nucleophilic addition of C = O or C = S bond (Chiche and Schweitzer 2017). The energy barriers for the addition of C = O and C = S by H₂O is 1.10 eV (Fig. 5, TS1) and 1.52 eV (Fig. S7, S-TS), respectively. Thus, the first step of COS hydrolysis will preferentially occur through the nucleophilic addition of C = O bond over Mg₂Al-Cl-LDH. Especially, it can be seen from the structure of TS1 that the chlorine ion also acts as Brønsted-base site and takes in one H atom from H₂O to form active hydroxy, and the hydroxy attack COS and activate C = O bond ultimately to form MTA (IM2a). The result is well in accord with the proposed reaction mechanism catalysed by hydroxy (George 1974; Zhao et al. 2013a). These results further confirm that the chloride ions in LDH can facilitate the activation and dissociation of H₂O, which is also supported by the adsorption configurations of reactants in Fig. 2.

For the second step of COS hydrolysis, the produced MTA (IM2a) will be easily dissociated to MT ~ HCl (IM2b) by nearby Cl ion with very low energy barrier of 0.05 eV (IM2a → IM2b, Fig. S5). The adsorbed HCl can easily turn and form the adsorption configuration of HT ~ HCl (TS2, IM3b) also with very low energy barrier of 0.15 eV. Then the hydroxyl in IM3b can rotate and form IM4b, and much higher resistance exists in the step with the activation energy of 0.79 eV (TS3b). Through the dissociation equilibrium of HTA (IM4b ⇌ IM4a ⇌ IM4c, Fig. S6), the IM4c can be produced with the maximum activation energy of 0.42 eV from IM4b to IM4a.

The last step for COS hydrolysis is the elimination reaction of sulfhydryl group in HT by the dissociated HCl. The C-S bond in HT will be broke after the HCl turns toward the S-H with the activation energy of 0.84 eV (TS4c). Then hydrogen transfer occurs from HCl to hydrosulphonyl, and the final hydrolysis products (H₂S and CO₂, IM5) will be generated and desorbed from LDH surface with small energy barrier of 0.17 eV (Fig. 4C). Meanwhile, the Cl ion is released from HCl to finish one catalytic cycle for COS hydrolysis.

By comparison, the transient states and activation energies of the reaction channels through the undissociated MTA and HTA for COS hydrolysis over the (0 0 3) face of Mg₂Al-Cl-LDH are also displayed in Fig. S8. Without the participation of Cl ions from IM2a to IM5, all the energy barriers of each step are much higher than that of the reaction path through the dissociated MT ~ HCl and HT ~ HCl. Specially, the activation energies of intramolecular hydrogen transfer from IM2a to IM3a and from IM4a to IM5 are 1.78 eV and 2.12 eV, respectively, which are even higher than that of COS hydrolysis in neutral water (Deng et al. 2007; Guo et al. 2016). The low adsorption energies as well as the hydrogen-bond interaction between MTA/HTA and LDH (Fig. 3 and Fig. 4) may confine the intramolecular hydrogen transfer without the help of Cl ions, which accounts for their high energy barriers.

Figure 5 The transient states and activation energies of the reaction channel through the dissociated MT~HCl and HT~HCl for COS hydrolysis over the (0 0 3) face of Mg₂Al-Cl-LDH. (Atomic legend: -Cl, -C, -S, -H, -O. The elements in layer of LDH are not shown.)

According to the above results, the reaction channels are presented in Fig. 6 for hydrolysis of COS through MT/HT or MTA/HTA. Comparing the high energy barriers through the route of MTA/HTA (TS2a, $E_a = 1.78$ eV or TS4a, $E_a = 2.12$ eV in Fig. S8), the energy barriers through the route of MT/HT are markedly decreased. The low energy barriers from IM2a to IM3b or from IM4a to IM5 are benefit from the participation of Cl ions in dissociative adsorption of MTA/HTA and subsequent hydrogen transfer process. The energy barriers for the rotation of hydroxyl in HTA or HT are close (TS3a, TS3b) because the Cl ions are not involved in any one of them. These results clearly demonstrate the COS hydrolysis will preferentially go through the dissociated intermediates of MT/HT ~ HCl. In the reaction channel, the rate-determining step of COS hydrolysis will be the nucleophilic addition of C = O bond in COS with the energy barrier of 1.10 eV, which is much lower than that of COS hydrolysis in neutral water (2.53 eV) (Deng et al. 2007).

In consideration of the dissociation of intermediates (Fig. 3 and Fig. 4) as well as the possible reaction path through the nucleophilic addition C = S in COS (Fig. S7), the total reaction networks of COS hydrolysis over the (0 0 3) face of Mg₂Al-Cl-LDH can be described in Fig. 7. In the reaction networks, the H₂O and COS are strongly coadsorbed on the surface sites of Mg₂Al-Cl-LDH. COS hydrolysis will follow the Langmuir-Hinshelwood reaction mechanism, and preferentially occur through the nucleophilic addition C = O instead of C = S in COS, which is also the rate-determining step. The dissociation equilibriums may exist among these adsorbed intermediates from IM2 to IM4, and the reaction routes through the dissociated intermediates will possess the lower energy barriers. The final products of H₂S and CO₂ can be easily desorbed from LDH surface with very low energy barrier of 0.17 eV.

2.4. The experiment results for COS hydrolysis over Mg₂Al-Cl-LDH.

The Mg₂Al-Cl-LDH was prepared for COS hydrolysis by coprecipitation method, and its structure and catalytic properties are shown in Fig. 8. All the peaks in the XRD pattern of Fig. 8A can be indexed as a rhombohedral structure with the typical (0 0 3), (0 0 6), (0 1 2), (0 1 5), (0 1 8), (1 1 0), and (1 1 3) reflections at $2\theta \approx 11.17, 22.47, 34.37, 38.33, 44.88, 60.24, 61.53^\circ$, respectively. And the interlayer spacing of (0 0 3) plane at $2\theta = 11.17^\circ$ is 0.79 nm, which is consistent with the other reported Mg₂Al-Cl-LDH samples (Guo et al. 2011; Yue et al. 2017). No other crystalline phase was detected, indicating the high purity of the as-synthesized Mg₂Al-Cl-LDH. The SEM image (Fig. 8B) of Mg₂Al-Cl-LDH also shows the typical nanosheet morphology with a diameter of 200–400 nm.

The catalytic performance of the Mg₂Al-Cl-LDH for COS hydrolysis is shown in Fig. 8C. The COS conversion increases rapidly above 50°C, and reaches 100% at 130°C. According to the Arrhenius plots as shown in Fig. 8D, the apparent activation energy for COS hydrolysis over Mg₂Al-Cl-LDH were calculated to be 85.6 kJ/mol (or 0.89 eV), which is close to the calculated theoretical value of 1.10 eV in Fig. 5. The

activity of the $\text{Mg}_2\text{Al-Cl-LDH}$ is much lower than that of $\text{MgAl-CO}_3\text{-LDHs}$ reported by Mi et al. (2019), which may be owing to the stronger alkalinity of intercalated CO_3^{2-} than Cl^{-1} (Liu et al. 2020). The FT-IR spectra were used to identify the accumulated intermediate products in the used $\text{Mg}_2\text{Al-Cl-LDH}$ after performance evaluation as shown in Fig. 8E. As for the fresh $\text{Mg}_2\text{Al-Cl-LDH}$, the multiple peaks in the range of $2800\text{--}3800\text{ cm}^{-1}$ and $470\text{--}1100\text{ cm}^{-1}$ can be assigned to the vibrations of surface hydroxy/ H_2O and metallic-oxygen lattice, respectively. Comparing with the fresh $\text{Mg}_2\text{Al-Cl-LDH}$, the multiple peaks of surface hydroxy/ H_2O in the range of $2800\text{--}3800\text{ cm}^{-1}$ strongly increase, indicating the strong adsorption of H_2O on $\text{Mg}_2\text{Al-Cl-LDH}$. The result is well coincident with the low adsorption energy of H_2O from -0.68 eV to -0.78 eV over the $(0\ 0\ 3)$ surface of $\text{Mg}_2\text{Al-Cl-LDH}$ as shown in Fig. 2. Meanwhile, very strong peaks around 1363 cm^{-1} appear, which can be attributed to the accumulated intermediate products including the MT, HT, or carbonate (Mi et al. 2019; Zhao et al. 2020). According to the data in Fig. 5, the activation energies from IM2a to IM4c through the route of MT/HT are much lower than that from IM1 to IM2a or from IM4c to IM5, which indicates that the accumulation of these intermediates in $\text{Mg}_2\text{Al-Cl-LDH}$ (e.g., MT and HT) is reasonable during COS hydrolysis. Besides, a small peak appearing at 1633 cm^{-1} after COS hydrolysis can be attributed to the bending vibrations of H_2O from the interlayer water (Yi et al. 2011), which accumulated in the used $\text{Mg}_2\text{Al-Cl-LDH}$ owing to its low adsorption energy of -0.78 eV as shown in Fig. 2A3. These results demonstrate that the experimental data of $\text{Mg}_2\text{Al-Cl-LDH}$ are well in accordance with the above theoretical calculations for COS hydrolysis.

3. Conclusion

In summary, the COS hydrolysis over model $\text{Mg}_2\text{Al-Cl-LDH}$ was studied to make clear the catalytic mechanism of intercalated chlorine anions as active basic sites by both theoretical and experimental methods. The adsorption of reactants at different sites on $(0\ 0\ 3)$ face of $\text{Mg}_2\text{Al-Cl-LDH}$ by DTF calculations found that the chloride ions in LDH can significantly activate the adsorbed H_2O to enlarge the $L_{\text{O-H}}$ and $\theta_{\text{H-O-H}}$ in H_2O from $0.98\text{ \AA}$ and 104.6° in original H_2O to $1.00\text{ \AA}$ and 110.9° in adsorbed H_2O , respectively. The adsorption of H_2O ($E_{\text{abs}}: -0.78 \sim -0.69\text{ eV}$) is much stronger than COS ($E_{\text{abs}}: -0.24 \sim -0.19\text{ eV}$), but H_2O and COS will still preferentially coadsorb ($E_{\text{abs}}: -0.81 \sim -0.86\text{ eV}$) on $\text{Mg}_2\text{Al-Cl-LDH}$ through the Langmuir-Hinshelwood mechanism for further hydrolysis reaction. Moreover, the Cl ions in LDH can function as the Brønsted-base sites to take in the H atoms from MTA/HTA and facilitate their dissociative adsorption to form $\text{MT/HT} \sim \text{HCl}$. The easy dissociation equilibrium may exist between MTA/HTA and $\text{MT/HT} \sim \text{HCl}$ on LDH owing to the low energy barriers ($< 0.5\text{ eV}$), and the dissociated $\text{MT/HT} \sim \text{HCl}$ will be the dominant intermediates on LDH with much lower adsorption energies ($-1.49 \sim -0.76\text{ eV}$) than MTA/HTA ($-1.42 \sim -0.69\text{ eV}$). The further research about the reaction channels found that the Cl ions also act as the Brønsted-base site and participate in the formation of transient states and subsequent hydrogen transfer process during COS hydrolysis to lower down the energy barriers. COS hydrolysis will preferentially go through the dissociated intermediates of $\text{MT/HT} \sim \text{HCl}$ with dramatically decreased energy barriers ($0.08 \sim 0.79\text{ eV}$) than MTA/HTA ($1.78 \sim 2.12\text{ eV}$), and the rate-determining step of COS

hydrolysis over $\text{Mg}_2\text{Al-Cl-LDH}$ will be the nucleophilic addition of $\text{C}=\text{O}$ in COS by H_2O ($E_a = 1.10$ eV). The experimental results showed that the activity of the as-synthesized $\text{Mg}_2\text{Al-Cl-LDH}$ increases rapidly above 50°C and reaches 100% COS conversion at 130°C with the apparent activation energy of 0.89 eV for COS hydrolysis, which is close to the calculated theoretical value of 1.10 eV. The accumulated intermediate products including the MT, HT, or carbonate can also be observed in the used $\text{Mg}_2\text{Al-Cl-LDH}$ by FT-IR with the very strong peaks around 1363 cm^{-1} , which is well in accordance with the theoretical prediction about the dissociative adsorption of MTA and HTA.

Declarations

Ethics approval and consent to participate: Not applicable.

Consent for publication: Not applicable.

Competing interests: The authors declare that they have no competing interests.

Availability of data and materials: All data generated or analysed during this study are included in this published article.

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Supplementary information: Partial data of adsorption and reaction were provided in the Supplementary Information file.

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Figures

Figure 1

The geometrically optimized model of $\text{Mg}_2\text{Al-Cl-LDH}$ unit cell (A1, A2) and its $(0\ 0\ 3)$ face with $p(2 \times 2 \times 1)$ supercells (B1, B2).

Figure 2

The geometrically optimized configurations of H₂O (A1-A3), COS (B1-B3) and H₂O/COS (C1-C3) adsorbed at the different sites on (0 0 3) face of Mg₂Al-Cl-LDH from top view with their adsorption energy labeled. (Atomic legend: -Cl, -C, -S, -H, -O, -Al, -Mg.)

Figure 3

The different geometrical configurations of MTA (A) and its two dissociative adsorption products of MT ~ HCl (B, C) on the (0 0 3) face of Mg₂Al-Cl-LDH from top view together with their adsorption energies labeled. IM2a ~ IM2c are the serial numbers of the possible intermediates during COS hydrolysis, which are labeled at the bottom right of each adsorption configuration. (Atomic legend: -Cl, -C, -S, -H, -O, -Al, -Mg.)

Figure 4

The different geometrical configurations of HTA (A1, B1), their possible dissociative adsorption products of $\text{HT} \sim \text{HCl}$ (A2, B2, B3), and the final hydrolysis products (H_2S and CO_2) adsorbed on the (0 0 3) face of $\text{Mg}_2\text{Al-Cl-LDH}$ from top view together with their adsorption energies labeled. IM3a ~ IM5 are the serial numbers of the possible intermediates during COS hydrolysis, which are labeled at the bottom right of each adsorption configuration. (Atomic legend: -Cl, -C, -S, -H, -O, -Al, -Mg.)

Figure 5

The transient states and activation energies of the reaction channel through the dissociated MT ~ HCl and HT ~ HCl for COS hydrolysis over the (0 0 3) face of Mg₂Al-Cl-LDH. (Atomic legend: -Cl, -C, -S, -H, -O. The elements in layer of LDH are not shown.)

Figure 6

The reaction channels for COS hydrolysis through the routes of MT/HT or MTA/HTA.

Figure 7

The total reaction networks including the intermediates of dissociated MT ~ HCl and HT ~ HCl for COS hydrolysis over the (0 0 3) face of Mg₂Al-Cl-LDH.

Figure 8

The structure and properties of the as-synthesized $\text{Mg}_2\text{Al-Cl-LDH}$. A) the XRD pattern of $\text{Mg}_2\text{Al-Cl-LDH}$, B) SEM image of $\text{Mg}_2\text{Al-Cl-LDH}$, C) COS conversion over $\text{Mg}_2\text{Al-Cl-LDH}$, D) Arrhenius plots of COS hydrolysis over $\text{Mg}_2\text{Al-Cl-LDH}$, E) the FT-IR spectrums of fresh and used $\text{Mg}_2\text{Al-Cl-LDH}$ samples.

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