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Synthesis of macroanion $[\alpha\text{-}SiW_{12}O_{40}]^{4-}$ as pillaring agents to layered double hydroxide Zinc-M^{3+}

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Abstract. Polyoxometalate intercalated layered double hydroxide was prepared by ion exchange of zinc-aluminum and zinc-chromium LDH with macro anion $[\alpha\text{-}SiW_{12}O_{40}]^{4-}$ at room temperature. The structural characterization was conducted with XRD, adsorption and desorption N_2 by BET method and FTIR analyses. An interlayer space of zinc-aluminum and zinc-chromium was increased after the intercalation process. The interlayer space at reflection (003) shows zinc-aluminum and zinc-chromium intercalated LDH is 10.36 Å and 10.49 Å from 7.57 Å and 7.68 Å, respectively. The value of surface area zinc-aluminum and zinc-chromium before intercalation are 2.10 m^2/g and 31.63 m^2/g and increase after intercalation to 14.0422 m^2/g and 128.87 m^2/g, respectively. This phenom identifies that both LDH has a great reflexibility based on anion in the interlayer.

Keywords: Polyoxometalate $[\alpha\text{-}SiW_{12}O_{40}]^{4-}$, layered double hydroxide, Zn-Cr, Zn-Al

1. Introduction

Layered double hydroxide (LDH) is a family of clay material that has positive charge with an interlayer space containing anion as counterbalance [1-3]. LDH can be written as $[M^{2+}_{(1-x)}M^{3+}x(OH)_2]^{(An-)}x/n{\bullet}nH_2O$ [4, 5]. LDH was formed by M^{2+} which is a metal cation divalent (e.g. Zinc (II), Ni (II), Cu (II), Co (II) and Mg (II)), M^{3+} is metal cation trivalent (Al (III), Cr (III) and Fe (III)) and A^{n-} is anionic (e.g. oxalate, citric, carbonate, nitrate, oxo-anion, acetic, aniline) [6-10]. LDH is well-known as an attractive mineral and has a high flexibility due to the exchangeable interlayer system [11]. Because of their ability, LDH is a considerable application in various sectors [2, 12], such as catalysis, pharmaceuticals, removal pollutant in water and also electrochemistry [13-15]. LDH is easy to synthesize [16], various methods are conducted to obtain LDH. Frequently, the methods used are co-precipitation and hydrothermal [17, 18]. Moreover, Djelali et al. reported that the nanoparticle of LDH has been synthesized by the sol-gel method. The nanoparticles LDH has extremely high interlayer anion exchangeability. So, their work represented the development of LDH potentials [19].

LDH has a low interlayer interaction and in recent decades, many of researchers have expanded the development of methods without breaking the basic structure [20, 21]. The main method adopts the reconstruction of layer and re-assembly anion in interlayers [17, 22]. Specifically, active species incorporation of materials, such as simple small-anions [23], macro-anions [24] and organic molecules [25] into the LDH interlayer space, which is an effective method of immobilization, and has been proved to be an effective source for increasing the efficiency and retesting a homogeneous system that is

corresponded [13, 26]. For example, Zha et al. reported that through the intercalation process, LDH nanosheets are intercalated by acetate anion for application as supercapacitors [27]. Zhang et al reported the intercalation of phosphotungstic acid into LDH by reconstruction method [28]. The intercalation of oxo-anions has been studied by interlayer space, although the gallery height is smaller [29]. Interlayer space can be more flexible based on the anion inhabits the interlayer.

As it is known, polyoxometalate is a metal oxygen cluster compound with a high oxidation state. Polyoxometalate are widely used as a catalysator, magnetic doped into porous materials, and this work is used as pillaring agent. Since Woltermann reported polyoxometalate intercalated was used as gases storage [30], polyoxometalate have been proven to be the substantial balancing for material applications [31-33]. In 2017, Zhang et al. reported the preparation of Mg/Al LDH intercalated by $[PW_{12}O_{40}]^{4-}$ has been enlarged from 0.77 Å to 10.8 Å [28]. Then, in 2019, Taher et al. have done POM-Ca/Al LDH intercalated with enlarged interlayer up to 0.16 Å [34]. In present work, we reported the LDH intercalated macro-anion $[\alpha\text{-}SiW_{12}O_{40}]^{4-}$ Keggin type by ion-exchange method. As we expected, after intercalating LDH-$[\alpha\text{-}SiW_{12}O_{40}]^{4-}$ the interlayer is more expanded then can be widely used as a highly effective application. XRD, BET and FTIR were then characterized on the obtained LDH.

2. Materials and method

2.1. Materials and instrumentation

The chemicals such as zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$), aluminum nitrate nonahydrate ($Al(NO_3)_3{\cdot}9H_2O$), chromium nitrate nonahydrate ($Cr(NO_3)_3{\cdot}9H_2O$), sodium hydroxide (NaOH), sodium carbonate (Na_2CO_3), sodium metasilicate (Na_2SiO_3), sodium tungstate dehydrate (Na_2WO_4), hydrochloric acid (HCl) and potassium chloride (KCl) were purchased from Merck and Sigma Aldrich. Deionized water was obtained from the Purite instrument, and the characterization were performed using XRD Rigaku Miniflex-600, BET (ASAP Micromeritics 2020) and FTIR Shimadzu FTIR Prestige- 21.

2.2. Synthesis of polyoxometalate $K_4[\alpha\text{-}SiW_{12}O_{40}]$

The synthesis of polyoxometalate $K_4[\alpha\text{-}SiW_{12}O_{40}]$ was conducted as follows: 0.65 g of sodium metasilicate was diluted by 10 mL deionized water called A solution. B solution was made by 11 g of sodium tungstate dehydrate was added into 20 mL boiled deionized water. HCl 4 M was prepared and added dropwise into B solution with a constant stirring. The synthesis temperature was kept at 313 K, mixed A and B solution for 30 min. Then, pH was adjusted to 5 before the temperature of synthesis was setting up at 373 K for an hour. Three mL of sodium tungstate 1 M and 5 mL of HCl 4 M were added quickly into the solution. When the solution was at room temperature, 3.5 g KCl was added, kept slowly stirring and heteropoly acid salt was obtained. Polyoxometalate $K_4[\alpha\text{-}SiW_{12}O_{40}]$ was characterized using XRD and FTIR [35].

2.3. Preparation of pillaring layered double hydroxide Zn-Al and Zn-Cr

Zn-Al and Zn-Cr layered double hydroxide synthesis is been reported by Palapa et al. using the co-precipitation method [36]. Layered double hydroxide was characterized using XRD, BET and FTIR. Zn-Al and Zn-Cr layered double hydroxide were prepared to modify using pillaring agent macro anion polyoxometalate $K_4[\alpha\text{-}SiW_{12}O_{40}]$ by ion-exchange method. As much as 1 g of layered double hydroxide is diluted with 50 mL of deionized water, in other batch, 10 g of polyoxometalate $K_4[\alpha\text{-}SiW_{12}O_{40}]$ was added to 50 mL of deionized water with vigorous stirring for an hour. After an hour, dropwise of the layered double hydroxide solution was added into polyoxometalate solution. To make sure the mixed solution has constant pH at 8, dropwise of sodium hydroxide 0.1 M was added while adjusting pH. Then, kept the solution at 60 °C for 24 h. Layered double hydroxide pillared by macro anion $[\alpha\text{-}SiW_{12}O_{40}]^{4-}$ was obtained and characterized by XRD, BET and FTIR.

3. Results and discussion

The XRD pattern and FTIR spectra of the starting materials zinc-aluminum and zinc-chromium are shown in figure 1. The XRD pattern of zinc-aluminum (denotes as a) and zinc-chromium (denotes as b) show the sharp and symmetric peaks, which is the typical characteristic of both LDH. The diffraction of LDH are 10° (003), 22° (006), 33° (009) and 60° (110). Barnabas et al. (2016) has reported the main diffraction peak that appears at diffraction angles of 11.4° (003), 23.3° (006), 34° (009) and 60.8° (110) [37]. The peaks that appear are characteristic of the material which has a layered structure. In addition, the intensity of the resulting diffraction peak is relatively weak and a broader peak. The result represented (figure 1a) that zinc-aluminum and zinc-chromium were successfully synthesized. The reflection of (003) identified the interlamellar space of LDH. The difference distances of interlamellar space are the effect of ionic radii of metal trivalent and divalent. However, the ionic radii of Al 0.53 Å and Cr 0.64 Å assume that the interlamellar space of zinc-chromium is greater than zinc-aluminum. The result shows the interlamellar distance of zinc-chromium 7.68 Å and zinc-aluminum 7.57 Å. Forano et al. reported that ionic radii affects the interlamellar space, based on the study about the differences in metal cation [38].

The FTIR spectra (figure 1b) of each spectrum has a similar broad vibration at 3400 cm^{-1} showing the vibration of OH in water molecule or OH in layers metal cation. The FTIR spectra zinc-chromium (denotes as b) shows impurities of anions in the interlayer. Broad and high vibration at 1385 cm^{-1} show the vibration of nitrate anion band and overlaps with carbonate anions band (in literature at 1370 [39]). Metal-oxide vibration is represented at under 800 cm^{-1}.

Layered double hydroxide intercalated using polyoxometalate $K_4[\alpha\text{-}SiW_{12}O_{40}]\bullet nH_2O$ was characterized by XRD and FTIR. The intercalation process of layered double hydroxide was carried out by co-precipitation method. The results of characterization are shown in figure 2. Figure 2a shows the XRD pattern of Zn-Al/[α-$SiW_{12}O_{40}$] (denotes as a) and Zn-Cr/[α-$SiW_{12}O_{40}$] (denotes as b). Zn-Al/[α-$SiW_{12}O_{40}$] and Zn-Cr/[α-$SiW_{12}O_{40}$] reflection (003) was shifted to lower 2 theta from 10° to 8°. (003) reflection was increased slightly to 10.36 Å and 10.49 Å, respectively.

The result of FTIR after intercalated is displayed in figure 2b. The strong, broad absorption vibration bands at 3400 are represented by OH vibration. In the case of polyoxometalate, has a unique vibration between 1000–800 cm^{-1} correspond to W=O, W-O-W and Si-O. This result is similar to Tyer et al. layered double hydroxide intercalated by polyoxometalate is observed at Si-O 926 cm^{-1}, W=O 980 cm^{-1}, W-Oc-W 881 cm^{-1} and W-Oe-W 780 cm^{-1} [34].

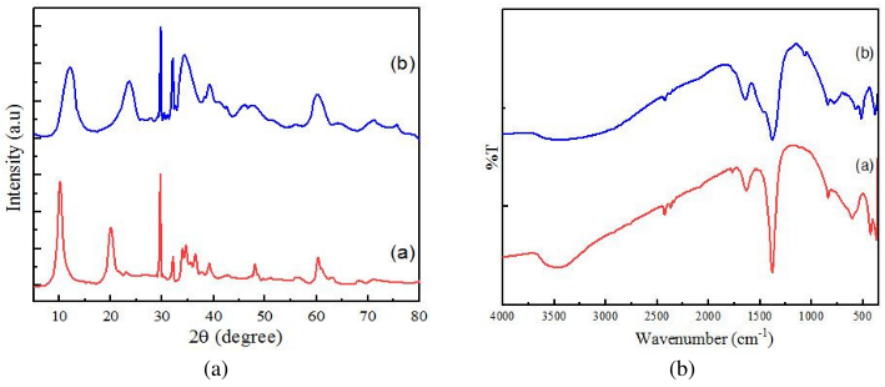

Figure 1. Characterization of zinc-aluminum and zinc-chromium layered double hydroxide (a) XRD and (b) FTIR spectra.

Zinc-aluminum, zinc-chromium and also intercalated materials have been studied by surface area analyses by BET method. Nitrogen adsorption-desorption isotherm are represented in figure 3 for all materials, the isotherm type was type IV. This type indicates the mesoporous with irregular pores. The classification of hysteresis based on IUPAC, for layer materials (like montmorillonite or clay minerals) [40] usually follows H3 hysteresis loop. H3 indicates the consistency with cavitation-induced evaporation, which is when the cavitation threshold exceeds the hysteresis loop (P/Po) > 0.42. The H3 hysteresis explains that the binding strength of polyoxometalate anion in interlayer is more than nitrate anion. The surface and pore size are followed by Zn-Al < Zn-Al/[α-$SiW_{12}O_{40}$] and Zn-Cr < Zn-Al/[α-$SiW_{12}O_{40}$] (the data is represented in table 1).

Table 1 shows that the surface area of zinc-aluminum and zinc chromium were slightly increased after the intercalation process. Zinc-aluminum was increasing sevenfold after intercalated by polyoxometalate K_4[α-$SiW_{12}O_{40}$]•nH_2O with pore size 15.67 nm. Zinc-chromium also increased

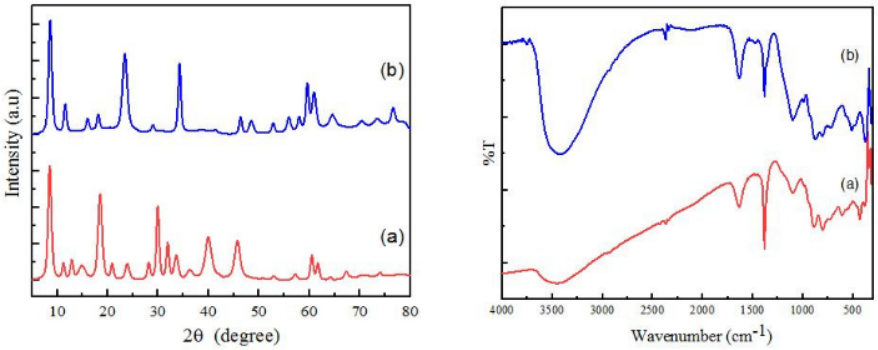

Figure 2. Characterization of zinc-aluminum and zinc-chromium intercalated by polyoxometalate K_4[α-$SiW_{12}O_{40}$]•nH_2O layered double hydroxide (a) XRD and (b) FTIR spectra.

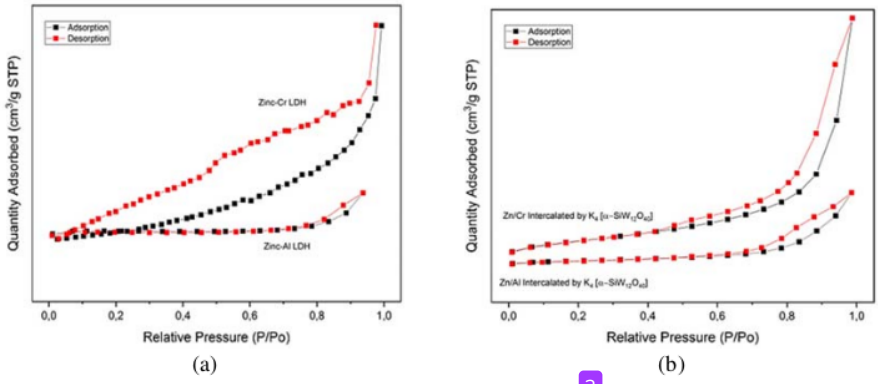

Figure 3. Isotherm linear plot of surface area analyses by (a) layered double hydroxide and (b) layered double hydroxide intercalated polyoxometalate K_4[α-$SiW_{12}O_{40}$]•nH_2O.

Table 1. Surface area data of layered double hydroxide and layered double hydroxides intercalated polyoxometalate $K_4[\alpha\text{-}SiW_{12}O_{40}]\bullet nH_2O$.

LDH	S_{BET} (m^2/g)	Pore size (nm)
Zn-Al	2.10	13.51
Zn-Cr	31.63	3.69
Zn-Al/[α-$SiW_{12}O_{40}$]	14.04	15.67
Zn-Cr/[α-$SiW_{12}O_{40}$]	128.87	3.69

from 31.63 m^2/g to 128.87 m^2/g with pore size before and after intercalating has no changed. According to IUPAC, these material are in the mesopore classification because the pore size are between 2–50 nm.

4. Conclusion

Zinc-aluminum and zinc-chromium was successfully intercalated by polyoxometalate $K_4[\alpha\text{-}SiW_{12}O_{40}]\bullet nH_2O$. The result of XRD pattern shows after intercalation 2 theta was shifted to a lower degree from 10° to 8°. The shift was followed by the slightly increase of interlayer distance. The interlayer distance of zinc-aluminum and zinc-chromium before intercalation are 7.57 Å and 7.68 Å to 10.36 Å and 10.49 Å, respectively. The FTIR data shows the unique diffraction of polyoxometalate is observed after intercalation at 1000–800 cm^{-1}. The surface area analyses shows the size of these materials is mesopore.

Acknowledgments

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