

Synthesis and Characterization of Zn Doped Magnesium Hydroxyfluoride, $Mg_{1-x}Zn_xFOH$.

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Abstract. A series of Zn-Doped Magnesium Hydroxyfluoride, $Mg_{1-x}Zn_xFOH$) samples with 0 to 0.15 of x were prepared using a sol-gel synthesis and dried with vacuum technique. XRD characterization of the samples indicated the amorphous phase of $Mg_{1-x}Zn_xFOH$ similarity with MgF_2 . The Zn doped in magnesium hydroxyfluoride did not affected on the basic structure of magnesium hydroxyfluoride. The FTIR spectra showed the samples had a broad band at $3000-3700\text{ cm}^{-1}$ and 1620 cm^{-1} was indicated of adsorbed H_2O molecules and a bridging hydroxyl groups, respectively. The intensity of the 460 , and 550 cm^{-1} bands correlates to Mg-F and Mg-O vibrations. The Zn-O stretching vibration of Zn-doped magnesium hydroxyfluoride appeared at 1634 and 621 cm^{-1} .

KEYWORDS: Sol Gel, Fluorolysis, Zn doped

INTRODUCTION

Metal fluoride is an inorganic compound that has an important role in the field of catalysis. For examples, dehydration reaction of d-xylose into furfural[1], ammoxidation of 3-picoline[2], liquid phase oxidation of ethylbenzene[3], dehydrohalogenation of 3-chloro-1,1,1,3-tetrafluorobutane[3], and acetylation of glycerol[4]. Preparation of metal fluorides catalyst has been developed primarily with a sol gel method. Sol-gel method has advantages such as homogeneity in the chemical composition, low temperature and low cost[5]. In the sol gel method, a solution undergo a phase change into a sol and then into a gel. Principally, two steps for the synthesis metal oxides from metal alkoxides are hydrolysis and condensation[6]. However, in the sol gel synthesis of metal fluorides, hydrolysis is replaced by fluorolysis[7]. Synthesis of metal fluoride is based on the reaction between the metal alkoxide with hydrofluoric acid followed by reaction with the replacement group fluorolysis OR by F[5]. This method has been successfully developed for the synthesis of magnesium fluoride. Synthesis of magnesium hydroxyfluoride can be done through a competition reaction between the hydrolysis reaction and methanolic fluorolysis using hydrofluoric acid[8]. In this paper, we reported the structure and properties of the material magnesium hydroxyfluoride with fluorolytic sol gel method. Zn doping is done to overcome the unstable of the Lewis acids catalyst where it mainly caused by moisture that involves water as a reactant, product or solvent[9]. Zn doping on the magnesium hydroxyfluoride to form $Mg_{1-x}Zn_xFOH$ have Lewis and Bronsted site can be application in catalysis reaction. The presence of Lewis and Bronsted site can give the high selectivity for catalysis reaction. Synthesis of the samples begin by dissolving anhydrous magnesium metal in methanol, followed by adding the aqueous hydrofluoric acid ratio of Mg:F is 1:1 and a precursor zinc acetate. This material was characterized by X-ray diffraction and Infra Red spectroscopy for the structure and the functional groups, respectively.

METHODHOLOGY

Materials

Magnesium turning (Sigma-Aldrich, 98%), Zinc acetate dihydrate (Sigma-Aldrich), Hydrofluoric acid (Sigma-Aldrich, 48%) and dried methanol (Sigma-Aldrich, 99%).

Synthesis of $Mg_{1-x}Zn_xFOH$ samples

Magnesium powder was dissolved in dried methanol at room temperature and refluxed at 70°C to prepared magnesium methoxide, $Mg(OCH_3)_2$ solution. A stoichiometric amount of HF 48% and Zinc acetate solutions was added to magnesium methoxide solution and mixed until a hydrogel was formed. The hydrogel was $Mg_{1-x}Zn_xFOH$ with x variations = 0; 0,025; 0,050; 0,075; 0,100; and 0,150 . The hydrogel was dried under vacuum at 70°C after aging process.

Samples Characterization

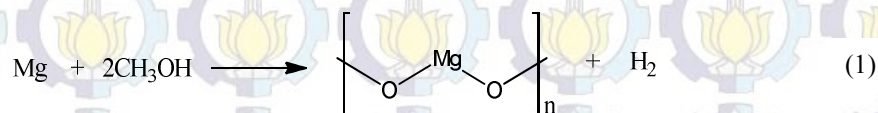
The structure of the samples was determined using X-ray Diffraction . XRD pattern were recorded on X'pert MPD X-ray diffractometer with CuK_{α} radiation (40 kV, 30 mA) in the 2θ range from 20 to 80°. The functional group of the samples was characterized by Fourier Transform Infrared (FTIR) spectrophotometer as pellets of KBr. Spectra were recorded between 4000 and 400 cm^{-1} on a Perkin-Elmer 2000 spectrometer in transmission mode.

RESULTS AND DISCUSSION

Synthesis of $Mg_{1-x}Zn_xFOH$

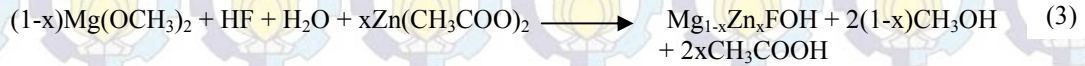
$Mg_{1-x}Zn_xFOH$ samples in this study were synthesized by sol-gel technique. Sol-gel technique have been known to produce a homogeneous product and take place at low temperature[10]. Precursors used in this research are magnesium metal, hydrofluoric acid (HF) as a source of F^- ions, zinc acetate as a source of Zn^{2+} , and dried methanol as a solvent as well as a source of alkoxide. The use of salt precursors such as nitrates, chlorides, and carbonates should be avoided because it will generate residual acid ions such as NO_3^- , Cl^- , and CO_3^{2-} which can reduce the stability of the colloid to form aggregates[11]. Magnesium metal precursors do not produce residual ions and easily react with methanol to produced magnesium methoxide (alkoxide). Metal alkoxides were fluorolytic further by adding a 48% aqueous HF solution. The Zn doping was conducted simultaneously during the sol-gel synthesis and was obtained a white gel.

Synthesis of $Mg_{1-x}Zn_xFOH$ with a sol gel method occurs in two stages. The first stage is the formation of metal alkoxides while the second stage is the polymerization process with HF. Phase formation occurs when the magnesium turning reacted with methanol anhyrous at 70 °C with reflux method. Heating is required at the time of reaction because magnesium is an alkaline earth metal that has low reactivity compared to alkali metals. The radius of the alkaline earth metal ions are generally smaller than the alkali metal so that the ionization energy required is greater. At the stage of making alkoxide, methanol is used so that all excess magnesium can react and form bubbles of gas produced from magnesium metal according to reaction :



Metal alkoxides characterized by a phase change from a solution into a white emulsion. Based on the equation 1, the reaction between magnesium turning with methanol would produce magnesium methoxide. Magnesium methoxide

formed is a necessary precursor to the synthesis of sol gel process. A metal alkoxide compound can prevent the precipitation during the synthesis sol gel which can be dispersed evenly. Magnesium methoxide as metal alkoxide then treated with 48% aqueous HF followed by Zinc acetat metanolic. At this stage, the hydrolysis reaction will competitive with condensation. Hydrolysis will replace the ligand (-OR) with a hydroxyl group (OH). In this step, condensation step not occurs but replaced by fluorolysis with substitution -OR ligand with F ion. The chemical pathway of the fluorolytic sol gel synthesis is given by equation 2.



According to equation 3, Mg^{2+} ion is replaced by Zn^{2+} ion on the network of the samples because the ionic radii of zinc and magnesium is also almost identical where ionic radii of Zn is 86 pm while ionic radii of Mg is 88 pm on the six coordination [12]. Doping is one of the synthesis process is done by mixing the direct precursors that are used with a certain composition ratio that aims to change or improve nature. The next step after hydrogel was formed is ageing process to form gel network more rigid, stronger, and shrink in the solution. Hydrogel was formed will settle on the bottom of the container with pure white color, while the upper layer was turbid solution. The upper layer solution and hydrogel were separated and dried by a vacuum pump at 70°C until a dried white powder was obtained which are $\text{Mg}_{1-x}\text{Zn}_x\text{FOH}$ solid.

Charaterization of $\text{Mg}_{1-x}\text{Zn}_x\text{FOH}$

The sample structures were characterized by X-ray diffraction (XRD) and the obtained XRD patterns are shown in Figure 2. The broad peak for MgFOH are observed at $40,5$; $34,5$; $53,5$; and 60° . These results still show similarities with diffractogram MgFOH. Peak at $2\theta = 40.5$ and 53.5° is a reflection of MgF_2 ★ with tetragonal structure. Peak at 34.5° , a typical peak of ZnO, ◆ having a bit shift with increasing Zn doping variation. The 2θ peak experiencing a shift towards increasingly smaller 2θ . This is due to the replacement of Zn^{2+} ions in MgFOH framework that led to the widening of the distance between the lattice. According to the Bragg equation, the diffraction angle is inversely proportional to the distance between the lattice. Diffractogram pattern $\text{Mg}_{1-x}\text{Zn}_x\text{FOH}$ also compared with the diffractogram pattern of $\text{Mg}(\text{OH})_2$. Figure 2 shows that the catalyst doping $\text{Mg}_{1-x}\text{Zn}_x\text{FOH}$ does not have a similarity with $\text{Mg}(\text{OH})_2$, ● at $2\theta = 59.06^\circ$. The peak appearing at $2\theta = 60.04^\circ$, ▲ indicating the presence of polymeric magnesium methoxide compounds which are still present in the catalyst framework doping (Scholz et al, 2012). Diffractogram pattern of all doping catalysts showed an amorphous phase with a peak width. Different amount of doping can be seen by calcination the samples at 350°C . At this temperature the methoxy group were lost and all samples show sharp peak. MgF_2 shows high crystallinity because this catalyst have high fluorin content ($x \geq 1$) so the reflection be increased. Meanwhile the diffractogram pattern form catalyst doping increasing from $x = 0$ to $x = 0,15$. Zn doping at $x = 0.1$ and $x = 0.15$ showed the increasingly sharp peak of ZnO, ◆ indicates the doping is maximum at framework. Besides that, Zn doping at $x = 0,025$; $0,05$; and $0,075$ do not show high peak for ZnO.

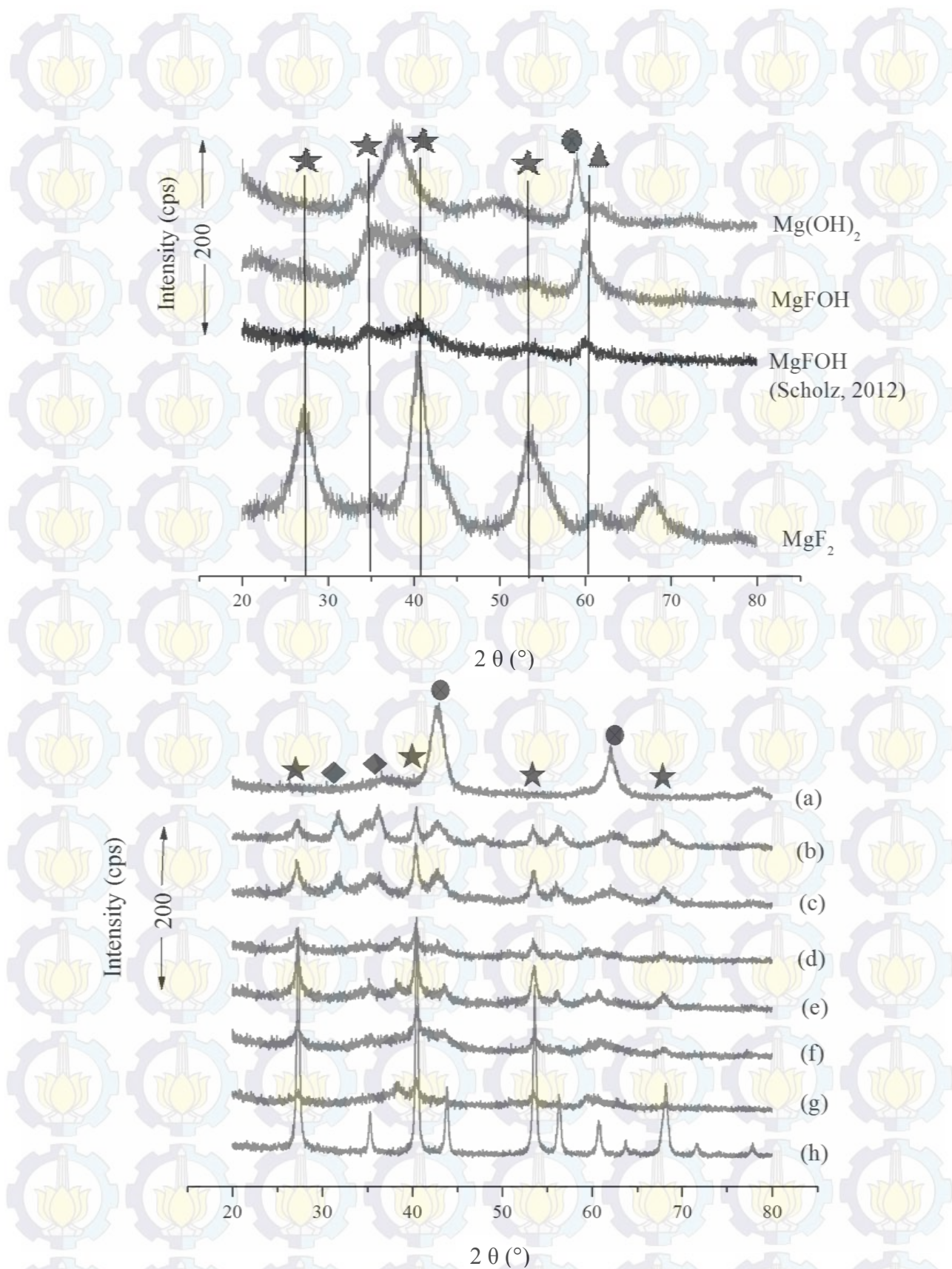


FIGURE 2. Diffractogram of samples before and after calcinations at $350\text{ }^\circ\text{C}$ (a) Mg(OH)_2 , (b) $\text{Mg}_{0.85}\text{Zn}_{0.15}\text{FOH}$, (c) $\text{Mg}_{0.9}\text{Zn}_{0.10}\text{FOH}$, (d) $\text{Mg}_{0.925}\text{Zn}_{0.075}\text{FOH}$, (e) $\text{Mg}_{0.95}\text{Zn}_{0.05}\text{FOH}$, (f) $\text{Mg}_{0.975}\text{Zn}_{0.025}\text{FOH}$, (g) MgFOH , (h) MgF_2

All samples were investigated by FTIR to clarify the vibration group. The presence of Bronsted acid groups can be seen from OH vibration bridging at $3500 - 3200 \text{ cm}^{-1}$ [13][14]. The infrared spectrum also provide information about the bond that is formed on the samples. In Figure 3, the vibrations are observed on the band of 3000 and 2750 cm^{-1} (CH) suggest the presence of a methoxy group reinforced with ν (CO) vibrations in the wave number 1080 cm^{-1} . Strong vibration also observed at 1460 cm^{-1} which is a vibration δ (CH_3) methoxy group. In addition, absorption band at $1400 - 1500 \text{ cm}^{-1}$ indicated the presence of bicarbonate compounds produced from the reaction of CO_2 with free hydroxyl groups on the surface of the sample [15]. Absorption band appeared at 1640 cm^{-1} and a broad band between 3675 and 3290 cm^{-1} related to water adsorbed on the surface of the sample [13]. The spectrum of $\text{Mg}(\text{OH})_2$ has a very strong band at 3700 cm^{-1} for OH group characteristic isolated of brucite [12]. Absorption band at 3700 cm^{-1} showed a decrease in the intensity of the bridge OH group in the sample. The Vibration of Mg-O and Mg-F is also observed at 550 and 460 cm^{-1} displayed in figure 4. Meanwhile, the metal doping on MgFOH samples were characterized by Zn-O stretching vibrations in the absorption bands at 620 and 1634 cm^{-1} [15]. Zn doping on the catalyst increase the Lewis acid site. Lewis acid can be definition as an acid that has an electron pair acceptor. It is caused by Zn^{2+} ion has lone pair orbital. Meanwhile Bronsted acid site obtained from MgFOH that has bridging interaction between F and Mg or Zn atom. Bronsted acid is an acid that can donate protons. The effect Zn doping on the catalyst will reduce the Bronsted acid site because Zn doping increase the Lewis acid site. Bronsted site and Lewis acid is very important in catalysis reaction such as isomerization, alkylation, asilation, esterification and many other reaction in industry.

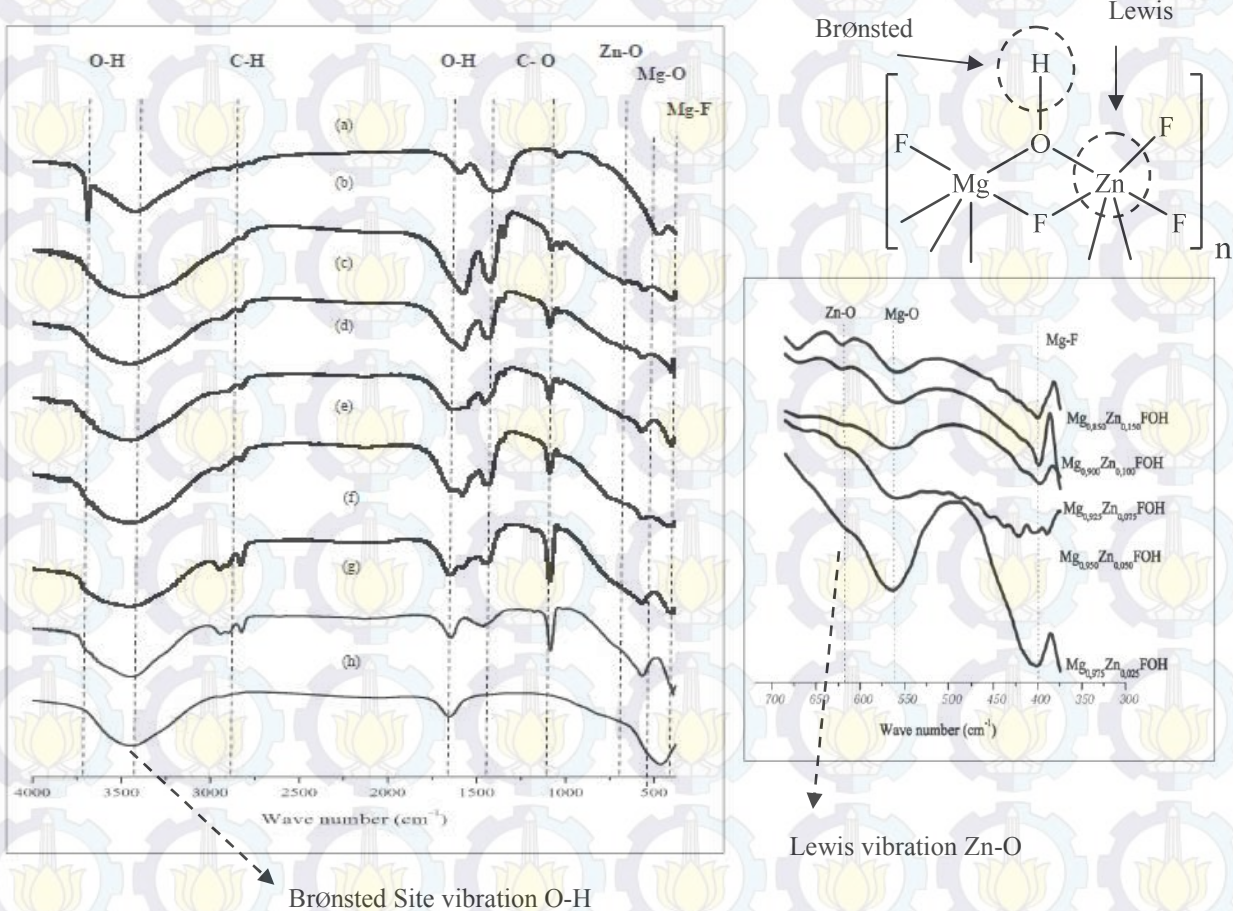


FIGURE 3. Infrared spectroscopy of catalysts (a) $\text{Mg}(\text{OH})_2$, (b) $\text{Mg}_{0,85}\text{Zn}_{0,15}\text{FOH}$, (c) $\text{Mg}_{0,9}\text{Zn}_{0,10}\text{FOH}$, (d) $\text{Mg}_{0,925}\text{Zn}_{0,075}\text{FOH}$, (e) $\text{Mg}_{0,95}\text{Zn}_{0,05}\text{FOH}$, (f) $\text{Mg}_{0,975}\text{Zn}_{0,025}\text{FOH}$, (g) MgFOH , (h) MgF_2 .

CONCLUSIONS

Sol-gel synthesis of metal fluoride $Mg_{1-x}Zn_xFOH$ with aqueous hydrofluoric acid produces amorphous phase. OH bridge is observed within the framework of the material shows Brønsted acid sites. Meanwhile, Lewis acid sites were obtained from doping Zn on MgFOH.

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