Characterization of a series Nickel Doped Magnesium Hydroxyflouride $Mg_{1-x}Ni_xFOH$ with XRD and FTIR

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Abstract. A series nickel doped magnesium hydroxyfluoride, $Mg_{1-x}Ni_xFOH$ has been prepared by fluorolytic sol-gel method. The x values in these series were from 0 to 0,15. The samples structure was obtained as amorphous phase from XRD characterization. The XRD patterns showed any peaks like the mixing between magnesium fluoride (selllaite) and magnesium hydroxide (brucite). The IR spectra from FTIR characterization of $Mg_{1-x}Ni_xFOH$ samples indicated the peaks of OH bridging at 3630-3000 cm^{-1} , Ni-OH vibration around 660-650 cm^{-1} Mg-O vibration around 550 cm^{-1} , and Mg-F vibration at 460 cm^{-1}.

1. INTRODUCTION

Several preparation method of catalysts have been developed that give breakthrough for development of catalyst synthesis, An example is a metal fluoride catalyst. Sol gel method was generally used for synthesis of inorganic metal fluoride because sol-gel method has effective route for obtaining these material[1]. As an example inorganic metal flouride catalyst is MgF_2. The sol-gel method based on the reaction between metal alkoxide and water in a suitable solvent followed by condensation to formed M – O – M bond. There is additonal sol-gel method has been known as fluorolytic sol-gel. In the fluorolytic sol-gel method, the reaction between metal alkoxide and anhydrous HF as replacment water at sol gel method (equation 1) [2]

$$M(OR)_n + nHF \rightarrow MF_n + nROH \qquad (1)$$

In the fluorolytic sol-gel method does not happen condensation reaction in the system[3]. Fluorolytic sol gel method was applied to synthesis magnesium fluoride (MgF_2) which have high flexibility concerning the synthesis parameter[4].

There are some methods used for MgF_2 synthesis. In this research, the synthesis of magnesium fluoride is modified by the replacment of several mole fluor ion,F^{--}, with hydroxy ion,OH^-. Hence, magnesium fluoride was changed to partially hydroxylated magnesium fluoride or magnesium hydroyfluoride. In this synthesis, anhydrous HF was replaced by aqueous HF according to equation 2[2][4]

$$M(OR)_n + (n-m)HF + mHOH \rightarrow MF_{n-m}(OH) \qquad (2)$$

This research also was synthesized nickel doped magnesium hydroxyfluoride to understand nickel effect on magnesium hydroxyfluoride.

The main purpose of this research was to study the influence of nickel addition on magnesium hydroxide fluoride's structure.

2. METODHOLOGY

2.1. Materials

Mg (98,8% turning, Sigma-Aldrich), Dry Methanol (99,9%,Merck), Nickel Acetate (99%, Sigma-Aldrich) and HF aqeous (48%, Merck)

2.2. Synthesis of Magnesium Hydroxide Fluoride

Magnesium hydroxyfluoride, $Mg_{1-x}Ni_xFOH$ with x = 0, 0,025; 0,05; 0,075; 0,10; 0,15 was synthesized by fluorolytic sol-gel method. Dried methanol was prepared to dissolve magnesium turning at room temperature and refluxed to obtain $Mg(OCH_3)_2$ solution. The stoichiometric amount of nickel was added to magnesium methoxide solution and mixed until green turbid solution was obtained. HF aqeous 48% with stoichiometry amount to this turbid solution and was stirred until hydrogel was formed. The hydrogel was dried under vaccum after aging.

2.3. Characterizations

The XRD pattern of nickel doped magnesium hydroxyfluoride were recorded with a X'pert Phillips X-Ray Diffractometter equipped with a Cu-K_α radiation in the range of 2θ between 20-80°.

The functional group of sample were determined by FT-IR. All samples pressed with KBr into clear pellet. FT-IR spectra were recorded in the range 4000-400 cm^{-1} with 8400S Shimadzu

3. RESULTS AND DISCUSSION

3.1. Synthesis

Magnesium hydroxyfluoride was synthesized using sol-gel method with magnesium methoxide as precursor. Magnesium hydroxyfluoride was formed when the ratio of Mg: F of 1: 1[4][5]. In this synthesis method, there were two steps that take place very quickly, namely hydrolysis and fluorolysis. Hydrolysis step occurred when 48% HF solution was reacted with metals methoxide[2][3]. Hydrolysis and fluorosis perform a very important role in shaping the structure of magnesium hydroxide fluoride according to equation 3

$$Mg(OCH_3)_2 + HF + H_2O \rightarrow MgFOH + 2CH_3OH \quad (3)$$

Hydrolysis occurs due to water whereas fluorolisis occur due to hydrofluoride acid in the HF solution.[6]. The hydrogels formed during fluorination[1] The obtained gel was dried under vacuum until was obtained free solvent solid. Similiar reaction happened when nickel (Ni^{2+}) added to synthesis procees to form the $Mg_{1-x}Ni_xFOH$. The value of x indicates the number of moles of nickel added[7]. The green hydrogel was formed as resulting nickel doping in magnesium hydroxyfluoride. These hydrogles were dried under vacuum condition. The free solvent green solid was obtained as $Mg_{1-x}Ni_xFOH$. Intensity of green colour of the solid depend on nickel amount.

3.2. Characterization of Samples

The XRD patterns (Figure 1) of all samples show very broad reflection indicating the presence of amorphous as well as the crystalline phase. The XRD pattern of magnesium fluoride observed as broad peak about 2θ 20,54; 27,26 and 40,68° and magnesium hydroxide observed asbroad peak around 2θ 33,17 and 55,68°. Similiarity XRD pattern for magnesium hydroxyfluoride and nickel doped magnesium hydroxyfluoride are given in figure 1. Magnesium hydroxyfluoride is intermediate brucite type structure of magnesium hydroxide and sellaite type structure of magnesium fluoride[8]. The nickel doping affects the structure of magnesium hydroxyfluoride. It can be seen from the diffractogram in figure 1 which shows that the increasing of nickel doping cause higher noise level and lower cristallinity of magnesium hydroxyfluoride. However, the nickel doping did not cause the appearance of typical peak of nickel oxide. This can be explained by the structure of magnesium hydroxyflouride tolerance against doping nickel. Ion radii of magnesium and nickel do not have significant differences.

The samples were characterized by FTIR (Figure 2). All samples show broad band between 3000 and 3700 cm^{-1} which indicated the presence of OH bridging in the solid. This is caused by hydrolysis and fluorolysis take place together. The absorbed water was confirmed by deformation of δH_2O vibration at absorption band at 1630-1650 cm^{-1}[4][9]. IR spectrum of $Mg(OH)_2$ shows a band at 3701 cm^{-1} which indicated to nonbridged OH[4]. The νCH vibration of some methoxy groups in all samples appears at 1080 cm^{-1} and 2950 – 2800 cm^{-1} [5][9]. In addition, the IR spectra of all samples show band at 1460 cm^{-1} indicated the νCO vibration which caused by carbonate groups on sample surface. There were weak band (660 -650 cm^{-1}) in IR spectra for $Mg_{1-x}Ni_xFOH$ with x= 0,05 up to 0,15

corresponding to Ni-OH vibration [10][11]. The vibration of Mg-O and Mg-F appear at band 550 cm^{-1} and 440 cm^{-1}, respectively.[9]

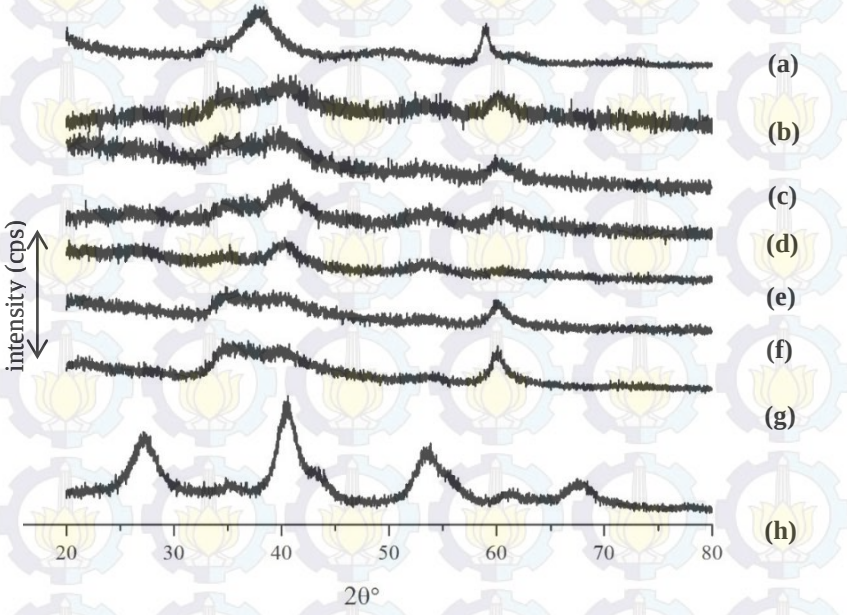

FIGURE 1. X-ray diffraction pattern of all sampls (a) $Mg(OH)_2$; (b) $Mg_{0,85}Ni_{0,15}FOH$; (c) $Mg_{0,90}Ni_{0,10}FOH$; (d) $Mg_{0,925}Ni_{0,075}FOH$; (e) $Mg_{0,95}Ni_{0,05}FOH$; (f) $Mg_{0,975}Ni_{0,025}FOH$; (g) MgFOH; (h) MgF_2

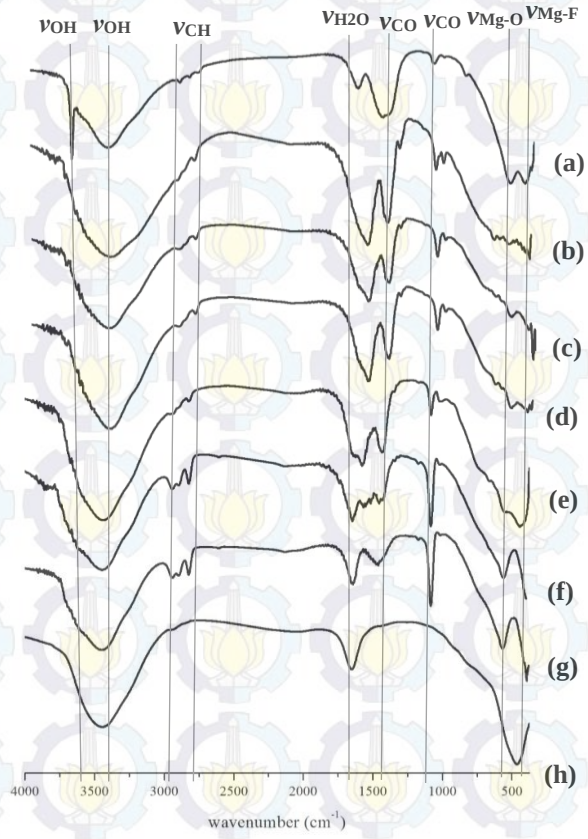

FIGURE 2.IR Spectra all samples (a) $Mg(OH)_2$; (b) $Mg_{0,85}Ni_{0,15}FOH$; (c) $Mg_{0,90}Ni_{0,10}FOH$; (d) $Mg_{0,925}Ni_{0,075}FOH$; (e) $Mg_{0,95}Ni_{0,05}FOH$; (f) $Mg_{0,975}Ni_{0,025}FOH$; (g) MgFOH; (h) MgF_2

4. CONCLUSIONS

It can be concluded nickel doped magnesium hydroxyfluoride, $Mg_{1-x}Ni_xFOH$ with x = 0,025; 0,05; 0,075; 0,10; 0,15 was synthesized succesfully by fluorolytic sol-gel method which have amorphous phase. Nickel doping gives effect to structure of magnesium hydroxyfluoride. All samples have OH bridging group.

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