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The Correlation Between Crystal Phase and Activity in Nickel Doped Zinc Fluoride Solid

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Abstract

Nickel-doped zinc fluoride ($Zn_{1-x}Ni_xF_2$) with x= 0; 0.025; 0.050; 0.075; 0.100 and 0.150 were synthesized from zinc acetate as precursors. Solid materials were prepared by the fluorolytic sol gel method. The resulting solid materials were characterized by XRD and FTIR. The XRD characterization of the samples showed that there were characteristic peaks of zinc fluoride, zinc oxide and zinc hydrogen fluoride. The IR characterization spectrum showed the presence of Zn-F, Zn-O and -OH bonds in the samples. Pyridine adsorbed FTIR technique explains that the material has Lewis and Brønsted acidity. The acidity site in the solid were influenced by the Zn-O and Ni-O bonds in the catalyst.

Keywords: Acidity site, fluorolitic, nickel doped, sol gel method

1. Introduction

Solid metal fluoride as a material that can play a role in various fields, one of which is catalyst [1]. When compared with metal oxides, metal fluorides have a more dominant level of surface acidity [2]. Several methods have been used in the synthesis of solid metal fluorides. Fluorolytic sol gel is a method that is in great demand because it produces products with high homogeneity at low temperature and requires low cost [3][4]. An example of a solid metal fluoride synthesized by the sol-gel method is ZnF_2 [5].

ZnF_2 were synthesized from metal oxide as precursors. Metal alkoxides are preferred as precursors in the sol gel method because it is suitable for hydrolysis reactions [6][7]. In this study, nickel metal doping was carried out on ZnF_2 to produce a solid with the formula $Zn_{1-x}Ni_xF_2$ which has acidic properties. Ni doping was carried out to overcome the acidity formed due to the reaction using the sol-gel method. The addition of nickel metal to the MgF_2 catalyst was able to increase the activity of the catalyst [8]. Variations in the amount of Ni added are 0.025; 0.05; 0.075; 0.1 and 0.15 moles. This number refers to the research conducted by Radityo et al [9].

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2. Procedure

a. Synthesis of sample

In this study, sol-gel method was used to synthesis solids $Zn_{1-x}Ni_xF_2$ with x = 0; 0,025; 0,05;0,075;0,1 and 0,15. The synthesis process was initiated by dissolving zinc acetate dihydrate with methanol at 85 °C under reflux conditions. The required amount for each nickel acetate was dissolved with methanol and added to the solution as dopant. Next, the HF solution (40%) was added and stirred until the solution was homogeneous. The result was aged until a stable gel was formed. Finally, the obtained solid was dried under vacuum and continued with the calcination process at 350°C for 5 hours.

b. Characterization of Sample

All synthesized solids were characterized by X-ray diffraction (XRD) using Cu-Kα radiation. Source (1.54Å) at 40 kV and 2θ = 20-80°. The obtained XRD pattern were compared with JCPS-PDF database. Fourier transform infrared (FTIR) spectra were recorded using an FT-IR Shimadzu spectrophotometer with KBr pellet in the range of 4000-400 cm^{-1}. Pyridine-FTIR spectra were recorded by FTIR spectrophotometer to study the acidity of solid materials.

3. Result and Discussion

a. Synthesis Results of The Fluorination of Zn Methoxide and Ni Acetate Mixture

Solid $Zn_{1-x}Ni_xF_2$ with X=0; 0,025; 0,5; 0,075; 0,1 and 0,15 were synthesized by the sol gel method. The sol gel method consists of two stages, namely hydrolysis and condensation. In this case hydrolysis is exchanged by the fluorolysis. The fluorolysis step occurs when zinc methoxide and nickel acetate react with HF as shown in equation 1.

$$1\text{-}x\ Zn(OCH_3)_{2(met)} + x\ Ni(CH_3COO)_{2(met)} + 2\ HF_{(aq)}$$
$$\downarrow$$
$$Zn_{1-x}Ni_xF_{2\ (s)} + 2(1\text{-}x)\ CH_3OH_{(aq)} + 2x\ CH_3COOH_{(aq)}$$

The hydrolysis step is followed by a fluorolysis reaction, resulting in a competitive reaction. The hydrolysis reaction occurs because the methoxy group is substituted by the F group of HF, while in the hydrolysis reaction the methoxy group will be substituted with the -OH group from water [10]. The gel formed from the fluorination reaction was allowed to form a more stable gel. The gel was dried by vacuum method to obtain xerogel. The obtained xerogel was further calcined at 350 °C to remove the solvent present in the solid [11]. The solids were characterized by XRD and FTIR.

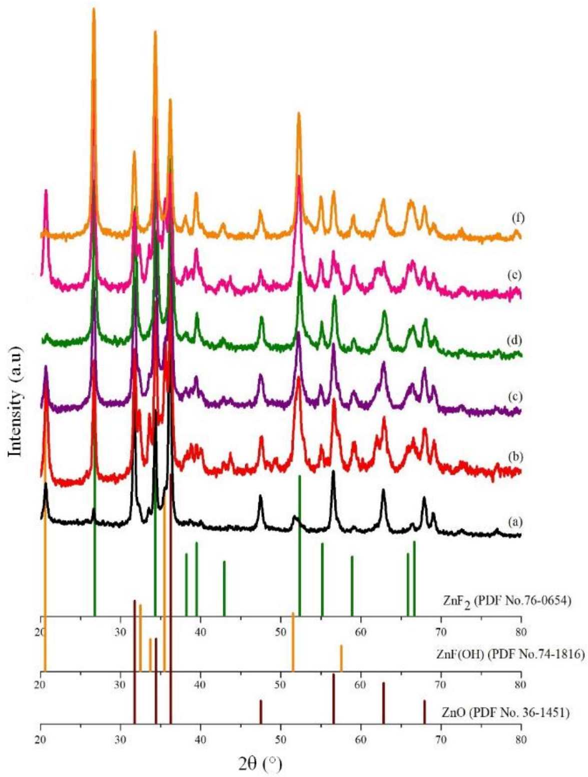

Fig 1. The XRD pattern of the fluorinated solid $Zn_{1-x}Ni_xF_2$ with x: (a) 0; (b) 0.025 (c) 0.050; (d) 0.075; (e) 0.100 and (f) 0.150 mol

b. Characterization of of the fluorinated solid $Zn_{1-x}Ni_xF_2$

The resulting $Zn_{1-x}Ni_xF_2$ with x=0; 0,025; 0,5; 0,075; 0,1 and 0,15 were characterizes by XRD to determine the crystal structure and the resulting pattern as shown in Fig 1. The resulting solids $Zn_{1-x}Ni_xF_2$ with X=0; 0.025; 0.05; 0.075; 0.1 and 0.15 were characterized by XRD and the resulting pattern as shown in Fig 1.

The XRD pattern shows the similarity of the solid peaks with the ZnF_2 database at 2θ=26.6; 34.4 and 51.6° and ZnO at 2θ=31.7; 36.1; 47.4 and 56.5° with tetragonal and hexagonal structures respectively. The presence of a ZnO peak formed could be due to the lack of moles of fluoride reacted with the precursor [12]. In addition, there is a peak at 2θ=20.06° which shows similarities to the ZnF(OH) database which has an orthorhombic structure. In the XRD pattern can be seen that there is a 2θ shift caused by metal doping on ZnF_2 so that there is a change in the lattice distance due to the difference in ionic radii [13].

Solid samples were also characterized by FTIR to know the chemical bonds in $Zn_{1-x}Ni_xF_2$ (Fig 2). All samples showed a band

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at 3517 cm^{-1} which indicated the presence of Zn-O-H band from ZnF(OH) compounds [14]. The absorption band at 3350 cm^{-1} indicates the presence of stretching O-H bonds. On the other hand, there are absorption bands at 1015 and 765 cm^{-1} which indicate the presence of O-H bonds which are due to the adsorbed water [14][15]. At wavenumber 520 and 418 cm^{-1}, it shows the presence of bonds of Zn-O and Zn-F respectively [15][16].

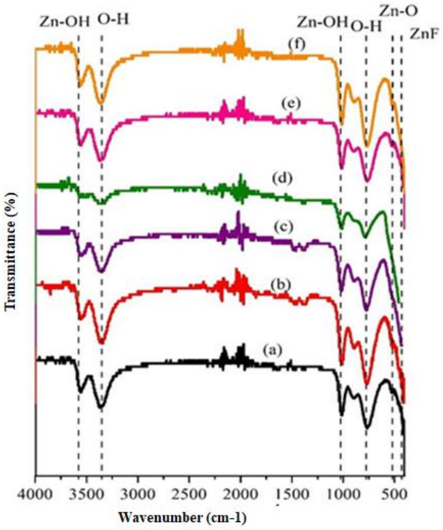

Fig 2. Fourier Transform Infrared (FT-IR) pectra of the fluorinated solid $Zn_{1-x}Ni_xF_2$ with a value of x = 0; 0.025; 0.050; 0.075; 0.100 and 0.150 mol

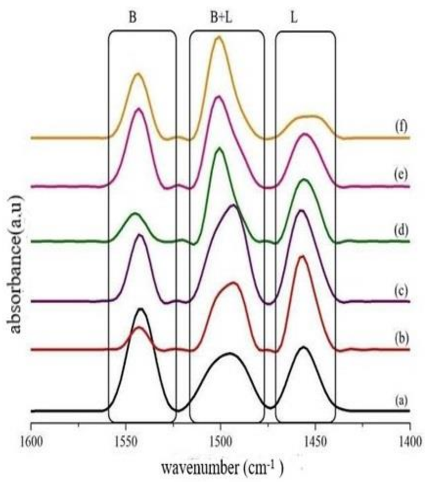

Fig 3. Pyridine adsorption-FTIR spectra of $Zn_{1-x}Ni_xF_2$ catalyst with doping variation (a) 0; (b) 0.025; (c) 0.050; (d) 0.075; (e) 0.100; and (f) 0.150 mol

The results of the acidity determination for nickel-doped zinc fluoride are shown in Fig 3. can be seen from this figure that there are 3 peaks formed at different wave numbers.

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The peak formed at wave number 1460-1450 cm^{-1} indicates an absorption which originates from the Lewis acid site on the materials surface, while the peak in the wave number in the range of 1540 cm^{-1} indicates absorption from the Brønsted acid site. Furthermore, the last peak seen is located at a wave number of around 1500 cm^{-1} indicating the presence of absorption from the Lewis and Brønsted acid sites [17].

Based on the calculation of the acidity of the solids, it shows that the Lewis acid site increases with the addition of Ni metal. The decrease in the Lewis acid site in the variation of 0.075 to 0.015, this is due to the maximum limit of the amount of Ni that can be accepted by the materials[18]. In addition, the decrease in the Lewis acid site is caused by the Zn-O bond which is easily formed when compared to Ni-O, so that the Lewis acid site is closed and the Brønsted acid site is increased. The Zn-O bond in the catalyst was confirmed through XRD analysis results, besides that it could be seen that there was an effect of the presence of ZnO on solid Fig 4.

4. Conclusion

Nickel-doped zinc fluoride has been successfully synthesized by the sol gel method to produce $Zn_{1-x}Ni_xF_2$ solids. The resulting solid is a mixture of zinc fluoride, zinc oxide and zinc hydroxide fluoride. The acidity site of solid were influenced by Zn-O and Ni-O bonds on the acidity of solids

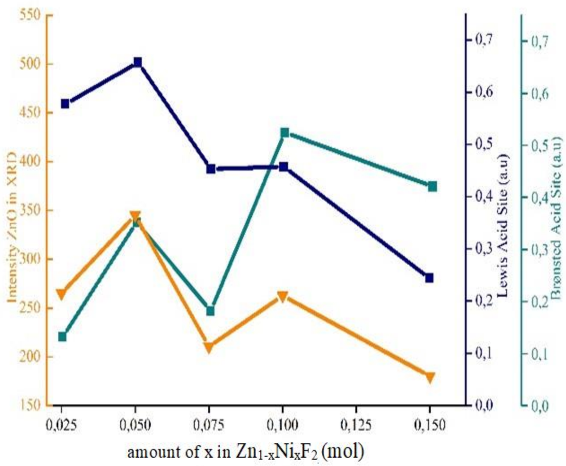

Fig 4. Correlation of ZnO (-▼-) intensity with Lewis (-■-) and Brønsted (-■-) acid sites

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