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PREPARATION, CHARACTERIZATION, AND THERMAL STABILITY OF B_2O_3-ZrO_2

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ABSTRACT

Synthesis of the borate-based compound with $ZrOCl_2$ to form B_2O_3-ZrO_2 has been conducted. The compound was characterized by FT-IR spectrophotometer, X-ray diffraction, acidity and thermal stability test. The results showed that the FT-IR main vibration spectrum of B_2O_3-ZrO_2 compound has appeared at wave number 401.2 cm^{-1} for Zr-O bonding vibration, 617.2 cm^{-1} for B-O-B bonding vibration and 910.4 cm^{-1} for B-O bonding vibration. The XRD diffraction pattern shows B_2O_3-ZrO_2 compound has an amorphous structure. The FT-IR spectrum after saturated with ammonia and potentiometric titration indicates that the compound of B_2O_3-ZrO_2 has acidic properties with a strong level of acidity. Thermal stability test shows that the B_2O_3-ZrO_2 compounds have high stability on temperature with increasing crystallinity after the compound was heated at 700 °C.

Keywords: B_2O_3-ZrO_2 impregnation, thermal stability.

INTRODUCTION

Non-metal doping of transition metal oxides is an interesting topic to develop novel materials based metal oxides. Non-metal doping with metal oxides has unique properties such as optical and electronic properties, crystal structures, and also the thermal stability of these compounds. The application of these materials is also can be used in many fields including catalysis, sensor, and photocatalysis (Marschall and Wang, 2014). One of the interesting element is boron due to metalloid properties and Lewis acidity of this element and compounds (Slack and Morgan, 2015). Boric acid is solid compound and has been applied as catalyst or support catalyst. The catalytic properties of boric acid are interesting due to chemical characters such as stability under high temperature and high stability. On the other hand, the acidity of boric acid is relatively low thus there is a limitation for application such as reaction with high acidity catalyst. In order to increase the acidity of boric acid, thus modification of boric acid is vital.

The various method has been applied for modification of boric acid to increase the acidity properties such as grafting, impregnation, and support with other material like metal oxides. For example, Osiglio and Blanco (2012) was prepared zirconium-boric acid and resulted in increased surface area of zirconium-borate after impregnation process. If surface area of materials is increased thus the catalytic activity of these materials is also increased due to reactivity of active side in materials. Boric acid supported metal oxide such as zirconium has been synthesis by Matsuhashi et.al (1994). Boric acid supported with zirconium oxide with 30% boric acid content can increase the acidity of boric acid to super acid. Super acid is the class of material with acidity is high than sulfuric acid. Boric acid supported zirconium oxide synthesized by Matsuhasi et.al was applied as an efficient catalyst for decomposition of ethanol to ethylene. This material has Hammett acidity value closed to -13 and acid than conventional acids such as nitric acid, hydrochloric acid, and sulfuric acid. Boric acid supported zirconium oxide also was prepared by Patil et.al (2002). Borat-zirconium from preparation has high thermal stability and can be used as a catalyst for high-temperature condition reactions. Previous research also reported that silica oxide was used as a support of boric acid to form B_2O_3-SiO_2 (Fitriana and Lesbani, 2017). This compound has high thermal stability up to 700 °C without changes structural properties. In this research, material B_2O_3/ZrO_2 was prepared in order to increase the properties of mixed boron compounds. Material B_2O_3/ZrO_2 was characterized by FTIR, XRD analyses, and acidity measurement by ex-situ analysis and potentiometric titration.

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EXPERIMENTAL SECTION

Chemicals and Equipments

Chemicals are used directly after purchased from Merck and Sigma Aldrich such as zirconium oxychloride, boric acid, ammonia, acetonitrile, and n-butylamine. Water was supplied from Integrated Research Laboratory using Purite water purification system.

The analysis was conducted using Shimadzu FTIR Prestige-21 with KBr pellet, and the sample was scanning of wavenumber 300-4000 cm^{-1}. XRD powder pattern was conducted using Shimadzu X-Ray LabX type 6000 and sample were scanning 1 $deg.min^{-1}$.

Preparation and Characterization of B_2O_3-ZrO_2

Preparation of B_2O_3-ZrO_2 was conducted according to Patil et.al (2014) with slight modification as follow. Zirconia oxochloride (48.3 g) was mixed with 110 mL water and 10 mL ammonia. The mixture was stirred for 30 minutes. pH of the mixture was checked. If pH mixture is less than ten thus ammonia was added to reach pH 10. The mixture was vacuum filtered and dry at 100 °C overnight (solid A). A separate experiment was conducted as follow. Boric acid (9.2 g) was dissolved in 200 mL water. Into this solution, solid A was added with slowly stirring for 1 hour. The mixture was vacuum filtered and dry at 100 °C for overnight. Characterization of material was conducted using FTIR spectroscopy,

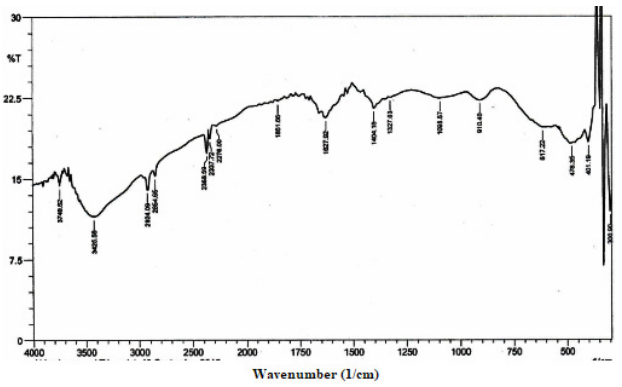

Figure 1. FTIR spectra of B_2O_3-ZrO_2.

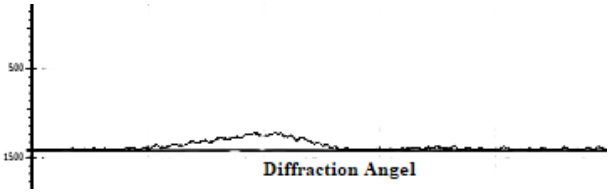

Figure 2. XRD powder patterns of B_2O_3-ZrO_2.

X-ray powder analysis, and acidity measurement using potentiometric titration.

RESULTS AND DISCUSSION

Compound B_2O_3-ZrO_2 was obtained as white bulk solid material. Characterization using FTIR spectroscopy as shown in Figure 2 demonstrated that vibration of boron and zirconia was appeared at wavenumber less than 1000 cm^{-1} (Ford, 2009). All peaks in the IR spectrum can be distinguished clearly although the spectrum is a little boardened. The main vibration of B_2O_3-ZrO_2 is appeared at 401.2 cm^{-1} (υ Zr-O), 478.4 cm^{-1} (υ O-Zr-O), 617.2 cm^{-1} (υ B-O-B), and 910.5 cm^{-1} (υ B-O). Other vibrations are identified as Zr-OH at 1404.2 cm^{-1} and 3425.6 cm^{-1} as O-H vibration. Vibration at 3425.6 cm^{-1} was broad and sharp due to synthetic of material B_2O_3-ZrO_2 was conducted in water. The FTIR spectrum indicated that material B_2O_3-ZrO_2 was formed but to clearly identified thus XRD analysis was conducted. XRD powder pattern of B_2O_3-ZrO_2 is shown in Figure 2.

XRD powder pattern of B_2O_3-ZrO_2 showed that broad diffraction peaks between 20-30 deg. Material B_2O_3-ZrO_2 is amorphous and no crystallographic parameter was identified. On the other hand, diffraction of zirconium oxide and boron oxide have crystallographic parameter, which was identified from crystalline sharp peaks. Zirconia oxide has main diffraction at 18-19 deg, 20-25 deg, and 28-33 deg. Boron oxide has diffraction at 15 deg and 28 deg (Atasoy, 2010). If material B_2O_3-ZrO_2 formed according to IR spectrum, then XRD pattern of B_2O_3-ZrO_2 should be clearly identified. Probably due to high water content in the material B_2O_3-ZrO_2 then diffraction peak was broad. Although material B_2O_3-ZrO_2 was kept at 100 °C overnight, but crystalline water cannot be removed by this way. Thus experiment was conducted using thermal stability test. Thermal stability test was conducted in range temperature at 300-700 to remove completely water from the material. Material was then characterized using XRD analysis as shown in Figure 3.

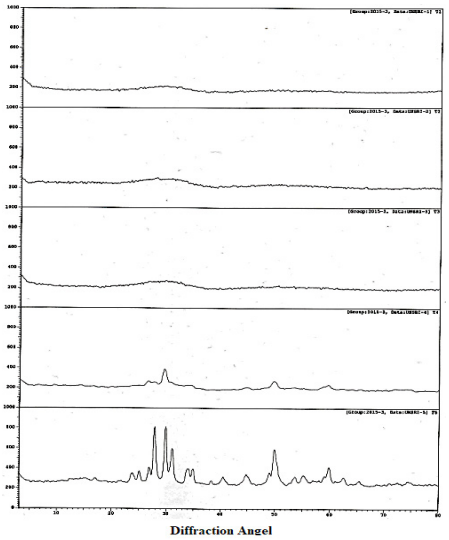

Figure 3. Diffraction patterns of B_2O_3-ZrO_2 at various temperatures A(300 °C), B(400 °C), C(500 °C), D(600 °C) dan E(700 °C).

Figure 3 showed that increasing temperature treatment could increase the crystallinity of material B_2O_3-ZrO_2. The temperature at 600 °C shows diffraction peak at 30 deg. Heating material B_2O_3-ZrO_2 at 700 °C was also increased crystallinity. Several peaks diffraction were detected after heating temperature 700 °C. Diffraction at 25-32 deg, 40 deg, 45 deg, 50 deg, 55-54 deg, and 60 deg was detected. Boric oxide was assigned at diffraction 25-50 deg and zirconium oxide was identified at diffraction 54-60 deg. From this results, the assumption of decreasing crystallinity due to water content as possible. This material B_2O_3-ZrO_2 was successfully synthesis at two phases i.e. amorphous phase at low temperature and crystalline phase at high temperature.

To investigate other properties of material B_2O_3-ZrO_2, thus acidity measurement was carried out using qualitative and quantitative analyses. Qualitative analysis of acidity was conducted as ex-situ using ammonia as probe and material were analyzed by FTIR as shown in Figure 4.

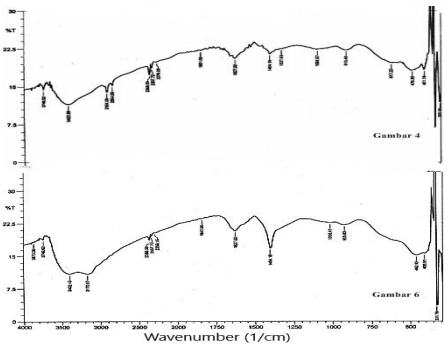

Figure 4. FTIR spectrum of B_2O_3-ZrO_2 (A) and B_2O_3-ZrO_2 after ex-situ exposes with ammonia (B).

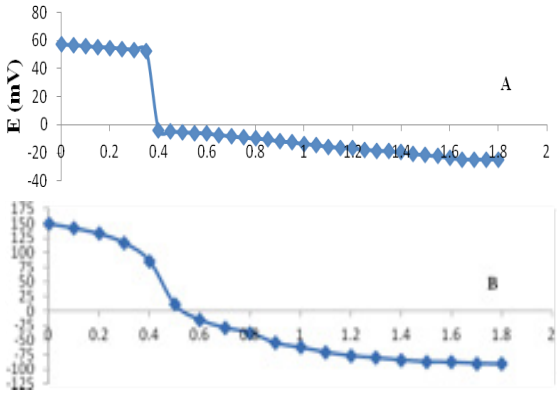

Figure 5. Potentiometric titration curve of H_3BO_3 (A) and material B_2O_3/ZrO_2 (B).

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Vibration at wavenumber 1404.2 cm^{-1} and 1627.9 cm^{-1} was appeared in material B_2O_3-ZrO_2 after ammonia exposes. These vibrations are assigned as ammonium ion which was chemisorption of Bronsted acid. Bronsted acid was detected and produced due to hydration of boric species (Sivaev and Bregadze, 2014). This material B_2O_3-ZrO_2 is classified as acid material. The strength of acidity of B_2O_3-ZrO_2 was measured using potentiometric titration. Titration curve of boric acid and B_2O_3-ZrO_2 is shown in Figure 5.

Titration was carried out using n-buthylamine. Titration curve in Figure 5 showed that H_3BO_3 has potential 57.2 mV and material B_2O_3/ZrO_2 has potential 149.3 mV. These results show material B_2O_3/ZrO_2 has strong acidity level than boric acid (Yu et.al, 2016). Thus material B_2O_3/ZrO_2 has acidity more than starting material and can be used as acid catalyst candidate for various chemical reaction.

CONCLUSION

Material B_2O_3-ZrO_2 can be easily prepared and has high crystallinity high temperature. Crystal structure of B_2O_3-ZrO_2 showed that amorphous phase at low temperature and crystal phase at high temperature. Material B_2O_3-ZrO_2 has high acidity than boric acid as starting material.

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