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Synthesis and Characterization of Zirconium Phosphate as a Solid Catalyst for Esterification of Wastewater Containing Acrylic Acid

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Abstract: Commercially available heterogeneous catalyst such as ion exchange resin has been used by the industry in the esterification reaction to overcome the problems caused by homogeneous catalyst. Heterogeneous catalyst with high tolerance to water is needed in the esterification of wastewater containing carboxylic acid. Zirconium Phosphate is one of the solid catalyst with the characteristics of high water tolerance and high thermal stability. In the present study, Zirconium Phosphate was used to catalyzed the esterification of wastewater containing acrylic acid. The catalyzed was synthesized using sol-gel method and characterized using X-Ray diffraction analysis (XRD), physisorption analyzer (BET surface area), thermal analysis (TGA) and Field Emission Scanning Electron Microscope (FESEM). This catalyst was proven to yield has high conversion and it can be reused without any treatment.

Key word: Esterification, catalysts, XRD, FESEM, zirconium, phosphate

INTRODUCTION

Homogeneous catalyst is used in the conventional method to accelerate the esterification reaction which consuming days to achieve equilibrium. In spite of the strong activity of these homogeneous catalysts, it imposed several drawbacks such as corrosion problems, difficult to be separated from reaction mixture and necessity to be neutralized after reaction (Jerny and Pandurangan, 2005; Izci and Bodur 2007; Akbay and Altioikka, 2011). Heterogeneous catalyst has been developed to overcome the aforementioned shortcomings. In addition, heterogeneous catalyst also can suppress the side reactions (Rattanaphra *et al.*, 2011; Akyalcin and Altioikka, 2012).

Ion exchange material is widely used as heterogeneous catalyst for the esterification reaction because of its' special characteristics such as insoluble, good selectivity and specificity. Park *et al.* (2009) studied on the water effect on esterification of oleic acid with methanol by ion exchange (Amberlyst 15). The reaction was carried out in batch reactor. The catalytic activity was decreased rapidly even water content was 1% of oleic acid due to the material adsorb water which poison the catalyst (Park *et al.*, 2009). The problems arise when the solid

catalyst is dissolved in water especially in aqueous media. Tetravalent Metal Acid (TMA) is one of the inorganic ion exchange with robust properties in thermal stability, chemical resistivity and ion exchange characteristics. These catalysts react as cation exchange using its' hydroxyl groups (H and -OH). Zirconium phosphate is important class in TMA which has been widely studied (Feng *et al.*, 2006; Jayswal and Chudasama, 2007; Patel *et al.*, 2008; Thakkar and Chudasama, 2009). It is a promising heterogeneous catalyst since it is thermal stable, tolerate to water and active in esterification reaction. It can be reused after recovering by a simple filtration (Kamiya *et al.*, 2004; Sinhamahapatra *et al.*, 2010).

Kamiya *et al.* (2004) studied the esterification reaction of acetic acid with ethanol in batch reactor using Zirconium phosphate as catalyst. The conversion is 20% after 2 h reaction at 343 K with catalyst loading of 0.8 g for 17.4 mmol of acetic acid. The catalyst was water tolerant and can be reused up to 5 times (Kamiya *et al.*, 2004). There are two different sites which may responsible for catalytic activities which are hydroxyl groups (Brønsted sites) and Lewis acid sites. The catalytic activity is not all controlled by hydroxyl group and the Lewis acid sites also play a role in the catalytic reactions. A large amount of water is being absorbed on the catalyst which shows

that the zirconium phosphate is hydrophilic but the limited of acid sites is surrounded by hydrophobic surface which avoids the water attacks (Alberti *et al.*, 2001; Asghari and Yoshida, 2006).

MATERIALS AND METHODS

Catalyst preparation: Amorphous zirconium phosphate was prepared by sol gel method. Zirconium chloride octahydrate ($ZrOCl_2 \cdot 8H_2O$) solution was added dropwise into the solution of sodium dihydrogen phosphate in the pH range 1-2 and $7^\circ C$. The molar ratio between zirconium chloride octahydrate and sodium dihydrogen phosphate (ZCO/SDP) was varied from 0.5 to 2.5 M. The gelatinous precipitates were continuously stirred for 1 h. Then, the solution was filtered and washed with ultrapure water to remove the chloride ions. The chloride ions were checked by 0.1 M argentum nitrate. The precipitate was dried at room temperature before it was sieved. The materials were converted to acid form by treating 1g of material with 10 mL of 1 M nitric acid for 30 min. The acid treatment was repeated for five times. The material was washed to remove adhering acid and dried at room temperature.

Characterization of the catalyst: The zirconium phosphate was characterized using X-Ray diffractogram ($2\theta = 5-80^\circ C$) to confirm the catalyst was amorphous. The thermogravimetric analysis was carried out at a heating rate of $10^\circ C \text{ min}^{-1}$. The surface area of the catalyst was determined by physisorption analyzer. The sample is degassed at $200^\circ C$ for overnight before analyzed. The surface morphology was captured using field emission scanning electron microscopy.

Esterification of acrylic acid with butanol: The esterification was carried out in three neck flask equipped with condenser, temperature controller and temperature probe. The molar ratio between acrylic acid and butanol was 1:3 and catalyst loading is 50%. The butanol was charged into the flask. After the temperature reached $100^\circ C$, the acrylic acid and catalyst was charged and the reaction time was started. The stirring rate was maintained at 500 rpm. The water was added to check the water effect to the catalyst. The product was analyzed using FID gas chromatography. The conversion of the esterification was analyzed using potentiometric titration.

RESULTS AND DISCUSSION

Catalytic performance: The catalytic performances of the synthesized zirconium phosphate with molar ratio of

ZCO/SDP ranges from 0.5 M to 2.5 M were screened using the acrylic acid esterification reaction. The conversion of acrylic acid was the indicator of the catalytic activity. Figure 1 shows all the catalysts yield similar conversion profile. The amount of phosphate loading has significant influence on the esterification of acrylic acid with butanol. Zirconium phosphate with molar ratio of ZCO/SDP 1 M has yield the highest for the first 4 h of the reaction. However, the conversion slightly drops after that and 20% conversion is observed after 12 h. On the other hand, zirconium phosphate with the molar ratio of ZCO/SDP 2 M has resulted a significantly high conversion among the others throughout the 12 h reaction and conversion of 50% is obtained after 12 h. The lowest conversion is given by zirconium phosphate with the molar ratio of ZCO/SDP 1.5 M; where the conversion of 10% is achieved after 12 h. The acidity nature of the catalyst has played a major role in determine the conversion of acrylic acid. The increase the catalytic activity is due to the higher acidic nature of the catalyst (Sinhamahapatra *et al.*, 2010). Zirconium phosphate 2 M was selected as catalyst for esterification of acrylic acid with butanol due its' best performance.

Catalyst characterization: The Zirconium Phosphate was confirmed amorphous by using XRD analysis with in 2θ range of 5 to $80^\circ C$. Figure 2 shows no sharp peak in the

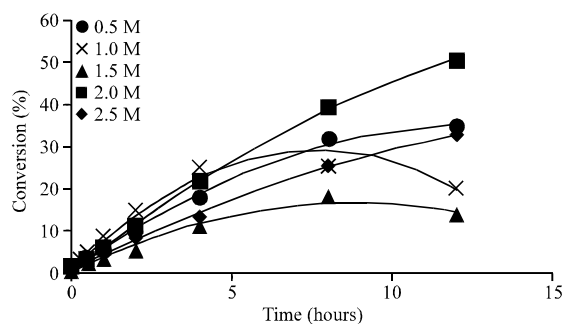


Fig. 1: Reaction profile (conversion) of the esterification of acrylic acid using zirconium phosphate with different phosphate loading

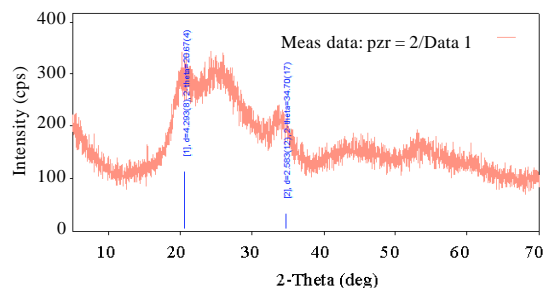


Fig. 2: X-Ray diffractogram

diffractogram and this indicates that the material possesses low crystallinity or the material is amorphous as elucidated elsewhere (Jayswal and Chudasama, 2007; Patel *et al.*, 2008; Moosavi *et al.*, 2009; Geng *et al.*, 2011). The materials obtained were white hard granules and the morphology was determined by FESEM Micrograph as in Fig. 3 shows that the Zirconium Phosphate had irregular particle shape, agglomerate (Fig. 3a) and very rough surface (Fig. 3b).

Thermo gravimetric (TGA) curve in Fig. 4 indicates that approximately 25% of total weight was lost as

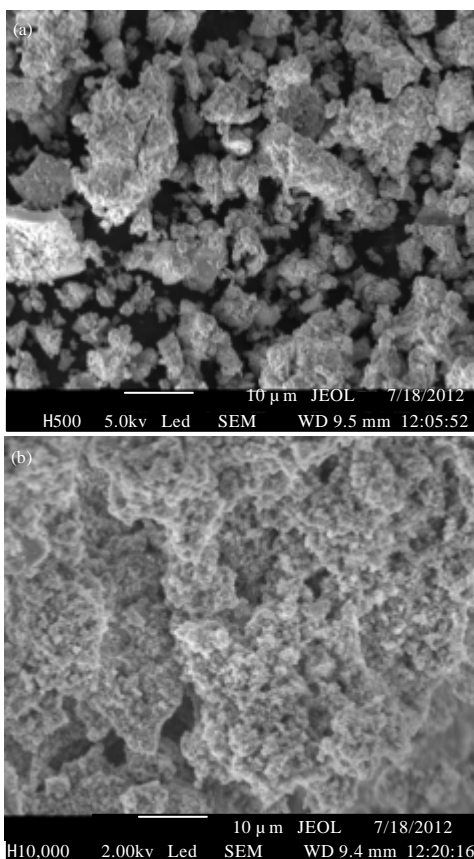


Fig. 3(a-b): FESEM micrographs. (a) 500 magnification; (b) 10000 magnification

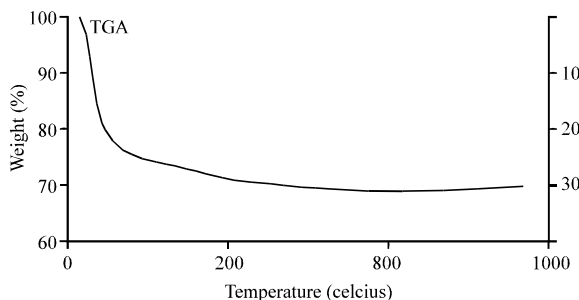


Fig. 4: TGA curve

temperature increases from room temperature to 100°C corresponding to the loss of moisture/hydrated water. The second weight loss is about 5% in the range of 200 to 600°C due to the condensation of hydroxyl groups. Beyond this temperature there is no weight loss observed until 950°C. Figure 5 represents the nitrogen sorption isotherm of Zirconium Phosphate. The surface area calculated using Brunauer Emmet Teller (BET) method is 170 m² g⁻¹.

Reusability: The reusability study performed at same condition as catalytic performance with the shorter reaction time 4 h. After the experiment, the catalyst was filtered to recover the catalyst from the reaction mixture. The recover catalyst was dried before reused for the same conditions. As can be seen in Fig. 6, the conversion had slightly decreased which showed that the Zirconium Phosphate had no significant deactivation after the third cycles.

Water tolerance: The water tolerant study was crucial to determine whether the catalyst was suitable for waste water treatment. The water was added initially to the reaction mixture. The esterification reaction conditions were same as catalytic conditions with shorter reaction time which was 4 h. The Fig. 7 shows the Zirconium Phosphate can withstand water up to 50% w/w.

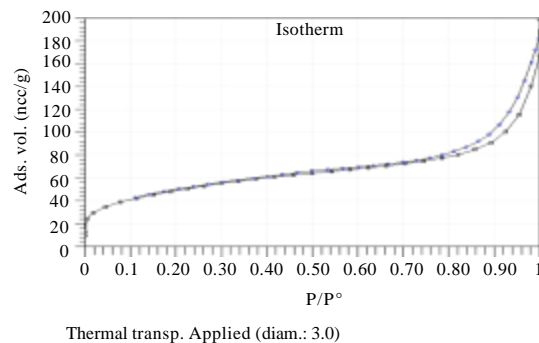


Fig. 5: N₂ sorption isotherm

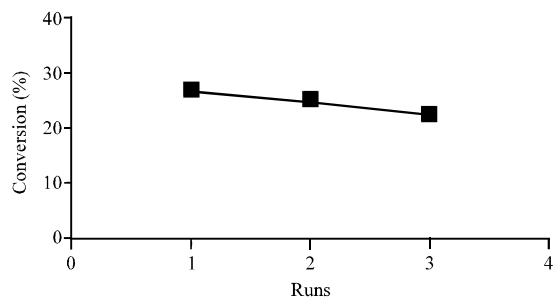


Fig. 6: Reusability of zirconium phosphate

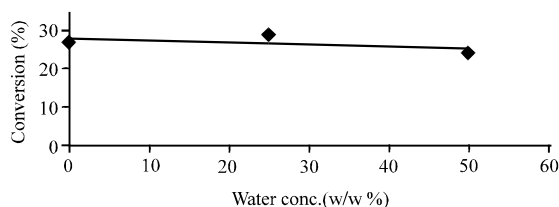


Fig. 7: The water tolerant towards zirconium phosphate

CONCLUSION

Zirconium phosphate possesses high surface area, good thermal stability and high water tolerance. The catalyst is suitable to be used for the esterification reaction of wastewater containing acrylic acid with butanol. The catalyst can be recycled for three times without significant loss of its catalytic activity.

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