Synthesis of PEG-monooleate using Cesium Heteropoly Acid as Heterogeneous Catalyst

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***Abstract*—Esterification of oleic acid with polyethylene glycol 600 (PEG-600) to produce polyethylene glycol monooleate (PEG-monooleate) has been studied in the presence of heterogeneous acid catalysts; cesium heteropoly acid (Cs HPA). The results were compared with current industrially used homogeneous acid catalyst; p-toluene sulphonic acid (p-TSA). The reaction was conducted under flow of nitrogen with vigorous stirring at 130 °C and the reaction was monitored at 1, 3, 7 and 24 hours. The results showed Cs HPAs exhibit 100% selectivity of PEG-monooleate from the first hour until 24 hours of the reaction time. Contrary to p-TSA catalyst, the formation of side product; PEG-dioleate was observed since the beginning of the reaction. Chemical and physical properties of catalysts were characterized using fourier transmittance infra-red (FTIR) and X-ray diffraction (XRD).**

Keywords—Heterogenous catalyst, Cesium heteropoly acid, oleic acid esterification , PEG 600, PEG-monooleate.

I. INTRODUCTION

Polyethylene glycol monooleate (PEG-monooleate) is usually synthesized via esterification of oleic acid and polyethylene glycol 600 (PEG-600). Among reported catalysts used in this reaction are homogeneous catalysts such as mineral acids; H_2SO_4, HI, HF, H_3PO_4, p-TSA and organic acid; HCOOH [1]. These homogenoous catalytic systems suffer problems due to 1) difficulties in recovering the catalysts after reaction completed, 2) product purification problem by generating huge amount of wastewater, corrosive catalyst that can lead to corrosion on reactor and pipelines, energy intensive and high cost [2]. Heterogeneous catalysts are much preferred catalysts since the reaction can occur under mild reaction condition, less energy intensive, easy separation of catalyst from product, high possibility to regenerate and reuse the catalyst. Example of heterogeneous catalysts reported are ZrO_2, TiO_2, SnO_2, sulfonic ion-exchange resin, sulfonic modified mesostructure SiO_2, sulfonated carbon-based catalyst, heteropolyacids (HPAs), aluminosilicates (mordenita, halloysite, kaolinite) and cation-exchange resins [3].This study covers the application of a heterogeneous catalyst; cesium heteropoly acid (Cs HPA) in the production of PEG-monooleate.

II. MATERIALS AND METHODS

A. Materials

Cesium chloride and heteropoly acid used were analysis grade (99%) for catalyst preparation. Oleic acid, technical grade (90%, Aldrich), polyoxyethylene of molecular weight 600 (PEG- 600) were used for reaction studies.

B. Methodology

The Cesium heteropoly acid (Cs HPAs) catalysts were prepared by wet-impregnation method. Cs HPAs were activated prior to reaction under vacuum at 100 ºC for 2 hours. The Esterification experiments were conducted under reflux in a standard-design glass apparatus where the temperature is regulated with silicon oil bath equipped with a temperature controller.

C. Characterizations

The X-ray diffraction measurements were carried out using Bruker D8 Advance Powder X-ray diffractometer (u–2u mode, Cu–Ka radiation at l = 1.5405 A, scintillation detector) equipped with EVA diffract software for data acquisition.

Both, -OH groups and acidity, were monitored by infrared spectroscopy. FT–IR spectra were recorded in the transmission mode using Bruker IFS66V/S spectrometer.

III. RESULTS AND DISCUSSION

A. Catalytic performances studies

Table 1 shows the heterogenous catalyst performance of 2.5% Cs-HPA (Cesium heteropoly acid) and 1.9% Cs-HPA were compared with homogenous catalyst of p-toluene sulphonic acid (p-TSA) and control reaction where the reaction was performed without catalyst. The reactions were performed at 24 hours with different Oleic acid and PEG 600 ratio.

Table 1 Esterification of oleic acid with polyethylene glycol 600 (PEG-600)

Catalyst	Oleic acid:PEG-600 = 1:1		Oleic acid:PEG-600 = 1:4	
	Conversion (%)	Selectivity (%)	Conversion (%)	Selectivity (%)
2.5% Cs-HPA	99.70	89.56	98.4	100.00
1.9% Cs-HPA	78.86	98.74	92.00	100.00
p-TSA	100.00	7.76	99.84	97.60
Control	71.15	92.79	79.74	100.00

Even though the homogenous catalyst *p*-TSA demonstrated complete conversion in Oleic acid: PEG-600 ratio at 1:1, the selectivity of PEG-monoolate is less than 10%. The Cs-HPA heterogenous catalyst series showed selectivity about 90% at the same ratio. However, the both homogenous and heterogenous catalyst showed similar catalytic activity when higher ratio of PEG-600 was used.

B. X-ray Diffraction and FT-IR Analyses

Fig. 1 shows X-ray diffraction patterns of 2.5% Cs-HPA and 1.9% Cs-HPA

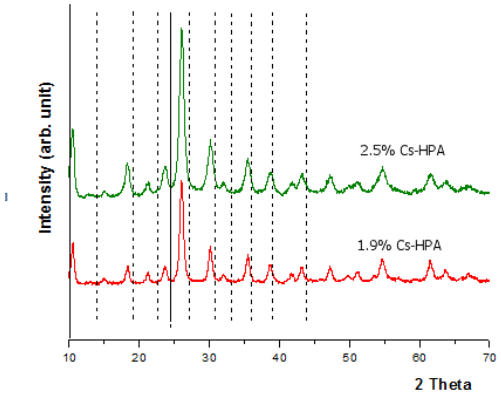

Fig 1. X-ray diffraction of Cs-HPAs catalyst

The Cs crystallinity 2θ showed 23° is increased with the additional of Cs metal content in the parent acid (heteropoly acid) as Cs 2.5 HPA intensity is higher compared to Cs 1.9 HPA. Four ranges of 2θ; 7º to 10º, 16º to 22, 25º to 30º and 33º to 38º are assigned as the peaks of HPA anions which depict as Keggin structure. The FTIR spectra further confirmed the structure of the prepared Cs-HPA compounds.

IV. CONCLUSIONS

It has been demonstrated that heterogeneous acid catalysts (Cs-HPA) are active and highly selective for the synthesis of PEG-monooleate even at low oleic acid:PEG-600 ratio.

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