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Oxidative desulfurisation of thiophenic compounds using nano Hap catalyst

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Highlights

- Hydroxyapatite (Hap) was synthesised from bone dust.
- Nano Hap was prepared by a green synthesis route
- Nano Hap was characterized by TEM, XRD, XRF, SEM , NH_3-TPD and BET
- Nano Hap and Hap were used as catalyst in oxidative desulfurization of TH, BT and DBT.

1. Introduction

The present world needs the use of environmentally benign fuels which contain organo sulfur compounds (TH, BT, DBT) to a specified low level [1]. Hydrodesulfurization(HDS) is the popular refining operation to remove sulfur compounds but it needs high severity of operation under the flow of hydrogen gas [2]. Hence to reformulate the process technology, catalytic oxidative desulfurization [3] can be chosen as one of the better choices because it can operate at near ambient temperature and pressure without the use of hydrogen [4]. Recently, hydroxyapatite (Hap) $\{Ca_{10}[PO_4]_6(OH)_2\}$is being investigated as an active catalyst or a catalyst support. It is the major inorganic compound found in bone or teeth and can be prepared by different sources. Wu et al. [5] prepared Hap from egg shell powders through heat treatment.

In the present work hydroxyapatite (Hap) prepared from bone dust was employed in the oxidation of thiophene (TH), benzothiophene (BT) and di-benzothiophene (DBT) and the maximum conversion reported were 46%, 35% and 12% for TH, BT and DBT respectively. Hap was converted to nano Hap by green synthesis route using different vegetable peals such as carrot, lemon, sweet potato and tea leaf extract and the catalyst was characterized with TEM, XRD, XRF, SEM , NH_3-TPD and BET surface area analysis. Finally the conversion of TH, BT, DBT were improved from 46 to 65%, 35 to 55% and 12 to 24% respectively, when nano Hap was used as a catalyst in place of Hap.

2. Methods

2.1. Hap preparation

Bone dust, collected from horticulture, was cleaned properly to make it free of unwanted substances,as far as practicable and dried to remove moisture and other volatile impurities, the resultant substance was pulverized to fine powder. Finally, the powdered sample was calcined at 600^0C for 2 h to prepare the Hap.

2.2 Nano Hap preparation

5 g of Hap powder was dissolved in 40 ml distilled water. Bio extracts were prepared by boiling 20 mins a mixture produced by taking different vegetable peals like carrot, lemon , sweet potato and tea leaf, 80 g of each separately , in 500 ml of distilled water. All the four extracts were filtered and 40 ml of Hap solution were added to 10 ml of each of those filtrates, separately and each stirred for 4 h. Aqueous ammonia (approx. 6 M) was used to maintain pH 10 for all the four solutions. These four Hap solutions were then placed together in autoclave at 150^0C for 72 h for hydrothermal transformation. Finally the autoclave was cooled at room temperature and the resulting solid product was rinsed with deionised water and dried at 60^0C for 24 h.

2.3 Oxidative desulfurization

Three types of model fuels were prepared whose compositions are as follows: Model fuel 1 [MF-1]: thiophene (500 ppm) in iso-octane; M odel fuel 2 [MF-2]: benzothiophene (500 ppm) in iso-octane; Model fuel 3 [MF-3]: dibenzothiophene (500 ppm) in iso-octane. A typical oxidation experiment was conducted using 40 ml model fuel and 0.06 g of catalyst, taken in a three necked round bottomed glass flask, housed in a water bath maintained at 50 ^{0}C with a digital temperature controller cum indicator with an accuracy of

±1^{0}C. The procedure was continued for 2 h under stirring at 1000 rpm. Samples (40 µL) were collected from the reaction mixture at every 10 min intervals. These samples were subsequently filtered to remove any trace of catalyst particle before these were analyzed in HPLC [Perkin Elmer, Series 200] with reversed phase Agilent SB C-18 column and a Perkin Elmer Series 200UV/VIS detector set at 254 nm. The mobile phase used was 90% methanol in water.

3. Results and discussion

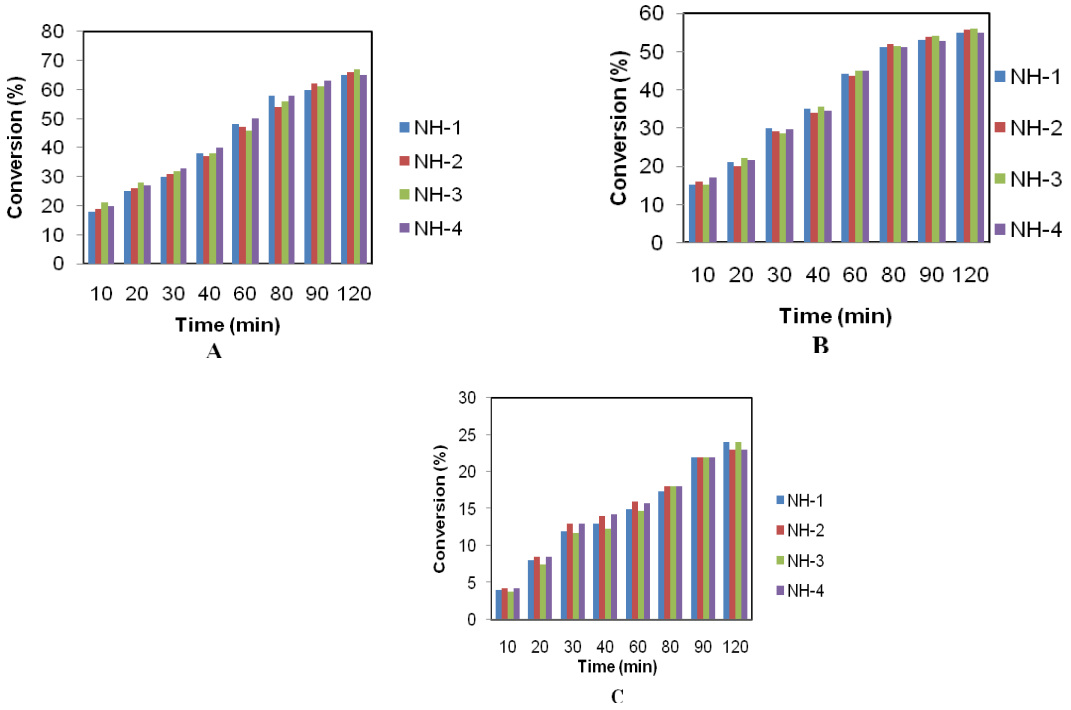

Figure 1. Catalytic efficiency of nano Hap for oxidation of (A)TH, (B) BT and (C) DBT

(NH-1: nano Hap from carrot peal extract; NH-2: nano Hap from lemon peal extract; NH-3: nano Hap from sweet potato peal extract; NH-4 : nano Hap fromTea leave extract)

(Sulfur concentration: 500 ppm; Stirrer speed: 1000 rpm; Operating temperature: 50 ^{0}C; Catalyst amount: 1.5 g/L; Model fuel amount: 40 ml; Catalyst particle size: 0.052mm; Reaction time: 120 min; Sulfur:H_2O_2 (mole ratio): 1:10)

4. Conclusions

Hydroxyapatite (Hap) was synthesised from bone dust and used in the oxidation of thiophene (TH), benzothiophene (BT) and dibenzothiophene (DBT) and TH recorded highest reactivity. Nano Hap was prepared by a green synthesis route, using vegetable extracts and showed significantly higher performance compared to Hap

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Keywords
nano hap particle, green synthesis route, oxidation.