

OXIDATIVE DESULPHURIZATION OF MODEL FUEL BY METAL IMPREGNATED Ti- β CATALYSTS

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Abstract - This paper showed the catalytic activity of Ti- β zeolite and how the metal impregnation on catalyst affects the efficiency of Ti- β on oxidation of benzothiophene (BT) and dibenzothiophene (DBT). Four metals (Ag, Cu, Sn and Mo) were chosen and impregnated on Ti- β zeolite at different concentration. The catalyst was characterised by BET, XRD and SEM analysis. Experimental results showed that the 2.5 weight% of Sn-impregnated and Cu-impregnated Ti- β zeolite have highest oxidation efficiency for BT and DBT respectively [66.68 % for BT and 60.92% for DBT] compared to Ti- β zeolite. Finally the effect of parameters like stirrer speed, temperature, oxidant mole ratio, catalyst loading and initial sulphur concentration on oxidation of BT and DBT with best metal impregnated catalysts was studied.

Keywords: - Ti- β , Oxidation, Benzothiophene, Dibenzothiophene, metal impregnation.

1. INTRODUCTION

The sulfur compounds in fuel causes generation of SO_x which in turn causes acid rain & air pollution also do harm to human health. Moreover causes poisoning of catalyst. Therefore removal of sulfur containing compounds from fuel has become a major environmental concern. Generally petroleum products are considered to contain four types of sulfur compounds namely alkyl benzothiophenes (~39%), dibenzothiophenes (DBT), alkyl DBTs (~20%) without substitution at 4 and 6 position, alkyl DBTs with substitution at 4 or 6 position (~26%)[1-3]. Thus, very stringent regulations for ultra-low-sulfur fuels were imposed on oil refineries to reduce the sulfur content of fuel oils to a very low limit about 10 to 20 ppm[4]. Normally industries apply catalytic hydrodesulphurization (HDS) technology for carrying out desulphurization. Oxidative Desulfurization (ODS) as an alternative process to the traditional HDS processes has gained much attention for deep desulfurization of fuels due to a number of reasons. In Comparison with conventional HDS process ODS has mainly two advantages. Firstly it can be carried out in liquid phase and can be operated under mild condition. Secondly the most refractory sulfur-containing compounds to the HDS process, (e.g. DBT and its derivatives) show high reactivity toward the oxidation by this method [5, 6]. Attached electron rich aromatic ring increases electron density at the sulfur atom which in turn causes electrophilic attack on the sulfur atom. Alkyl groups attached to the aromatic ring also contributes an increase in electron density. Thus, the

intrinsic reactivity of molecules like 4,6-dimethyl DBT is substantially higher than that of DBT, and in fact the sequence of increasing susceptibility to oxidation is exactly opposite to that to HDS[7]. Besides, the ODS process is a non-hydrogen consuming desulfurization method and can be applied whenever enough hydrogen sources are not available. By ODS process, these refractory sulfur compounds are oxidized to their corresponding sulfoxides and subsequently sulfones which can be removed by a number of separation processes including solvent extraction, adsorption, etc.

2. Experimental Methodology

2.1 Catalyst Preparation

Ti- β was synthesized according to the procedure reported in literature[8]. Synthesis of titanium-beta requires two solutions, solution A and solution B. Solution A was prepared by adding 0.58 g of tetrabutylorthotitanate to 4.0 g of distilled water and to the resulting suspension was added 2.0 g of H₂O₂ after 1 h. The mixture was stirred at room temperature for 1 h, leading to solution A containing peroxide titanate. Solution B was prepared by dissolving 0.0124 g of anhydrous NaAlO₂ and 0.015 g of NaOH in 8.0 g of tetraethylammonium hydroxide (TEAOH) at room temperature with 1 h stirring. Solution A and B are mixed together and stirred for 1.5 h. A clear homogeneous solution obtained after 2 h was heated to 353 K and dried while stirring. When the gel became dry to solid, it was ground to fine powder and transferred into a teflon beaker situated in a teflon lined special autoclave, where water (5.0 g), as a source of steam was poured at the bottom. The crystallization was carried out in steam at 403 K for 96h, subsequently at 448 K for 18 h under autogenous pressure. The recovered product was washed with distilled water, dried at 308 K for 10 h, and calcined at 793 K for 10h in the flow of air. The resulting Ti-beta zeolite was treated with 1 M H₂SO₄ at room temperature for 12 h and then washed with distilled water, dried at 308 K for 10 h, and calcined at 793 K for 5 h under the air flow. The prepared Ti- β catalyst was impregnated with varying loading of metals. Impregnation was carried out by taking catalyst in the aqueous solution of salt of the metal and then stirring the mixture under heating until the whole mixture gets completely dry. The mass was then washed, dried and calcined at 500°C for 5h. Finally Ti- β catalyst impregnated with varying loading of different metals was obtained.

2.2 Reaction Methodology: The reaction was carried out in a 100 ml glass reactor fitted with a glass stirrer and condenser, kept in a water bath whose temperature was maintained within $\pm 1^\circ\text{C}$ accuracy by using a temperature controller cum indicator. A typical reaction was carried out by taking 50 ml of model fuel, a definite amount of catalyst and TBHP (TBHP:S=10:1 mole ratio) in the reactor at various temperature under stirring at various speeds. Reaction samples were taken out at 10 minutes of time interval. The samples were analyzed in high performance liquid chromatography (Perkin Elmer, Series 200) with reversed phase Agilent SB C-18 column and conversion was determined.

3. Results

3.1: Catalyst Characterization

XRD analysis: XRD analysis of Ti- β was performed. Fig.1 shows the XRD plot. From the XRD plot it is clear that the prepared catalyst is crystalline in nature.

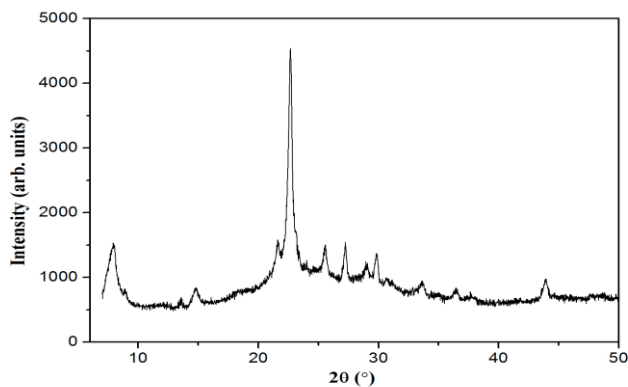


Fig.1: XRD plot of Ti- β catalyst

SEM and HRTEM images of Ti-beta zeolite

The scanning electron microscopy (SEM) image of calcined Ti-beta catalyst is shown in Figure 2. The Ti-beta sample appears to be highly crystalline with uniform crystal size and no amorphous phases detected on the surface. Ti-beta nanoparticles with regular shape can be clearly observed in the high resolution transmission electron microscopy (HRTEM) image (Figure 3) of calcined sample. The crystal size of the synthesized Ti-beta calculated from HRTEM image is in the range of 20-40nm. The chemical compositions of Ti-beta sample are listed in Table 1 based upon the EDX results.

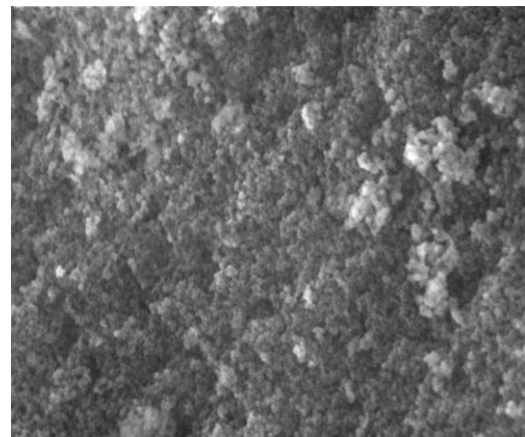


Fig.2 SEM image of Ti- β catalyst

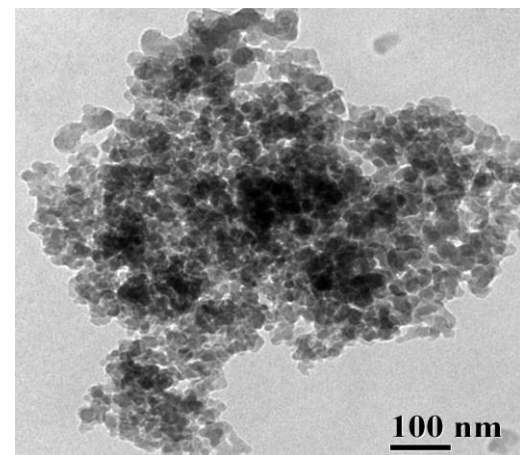


Fig.3 HRTEM image of Ti- β catalyst

BET of Ti- β zeolite

The multipoint Brunauer Emmett Teller (BET) analysis of the catalysts has been done by Quantachrome-Autosorb-1 (Model: AS1 MP/Chemi-LP). In the determination of specific BET surface area (SBET), the adsorbate gas used is nitrogen since it is inert and does not react with the solid catalyst. The samples were degassed at 200°C for 15 min and 2 h under high vacuum before the adsorption of nitrogen at 196°C was performed. The P/P0 (where P is the equilibrium pressure and P0 is the saturation pressure of the adsorbate gas at the adsorption temperature) tolerance is maintained at a value of 6. Result of BET analysis is given in Table 2.

Catalyst	Avg pore radius(\AA)	BET surface area (m^2/g)	Total pore volume(cc/g)
Ti-beta	124.18	55.965	0.345

Table 2: BET analysis of Ti-beta zeolite.

Catalyst	Ti/(Si+Ti+Al), mol%	Na/(Si+Ti+Al), mol%	Al/(Si+Ti+Al), mol%
Ti-beta	3.115	0.616	0.445

Table 1: Chemical composition of Ti-beta zeolite.

3.2: Experimental Results:

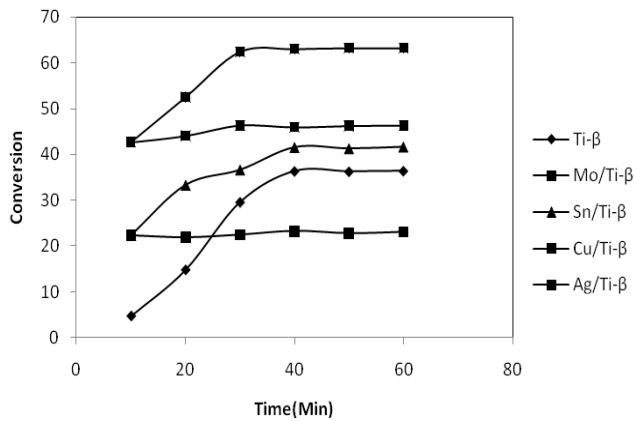


Fig 3: conversion of BT with 1.5% metal impregnated Ti-β

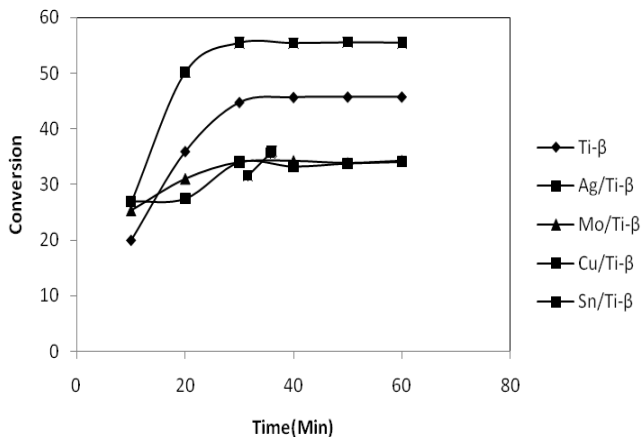


Fig 4: conversion of DBT with 1.5% metal impregnated Ti-β

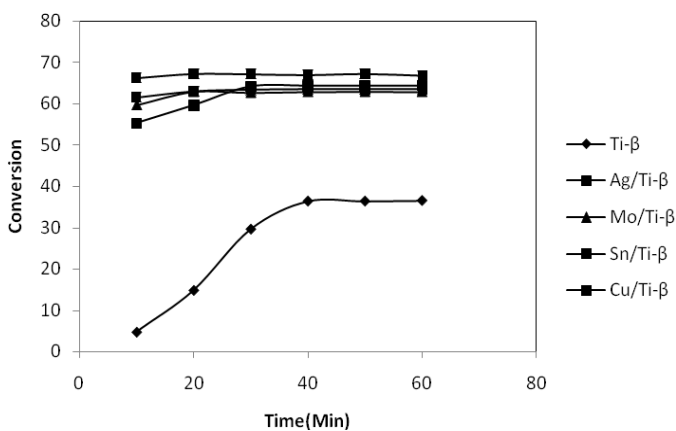


Fig 5: conversion of BT with 2.5% metal impregnated Ti-β

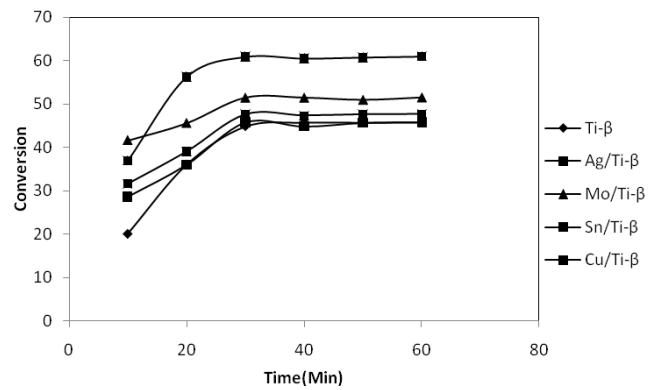


Fig 6: conversion of DBT with 2.5% metal impregnated Ti-β

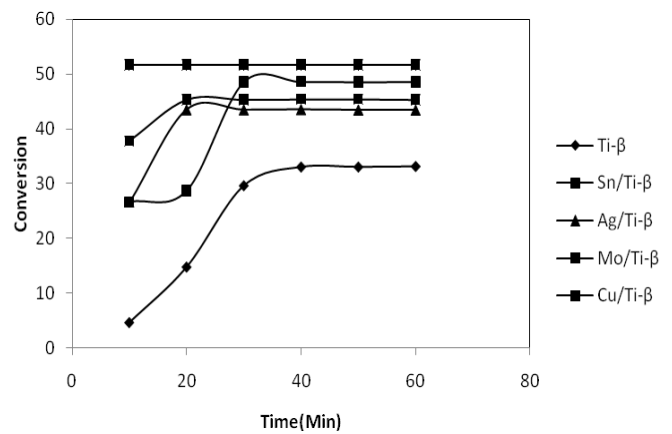


Fig 7: conversion of BT with 4% metal impregnated Ti-β

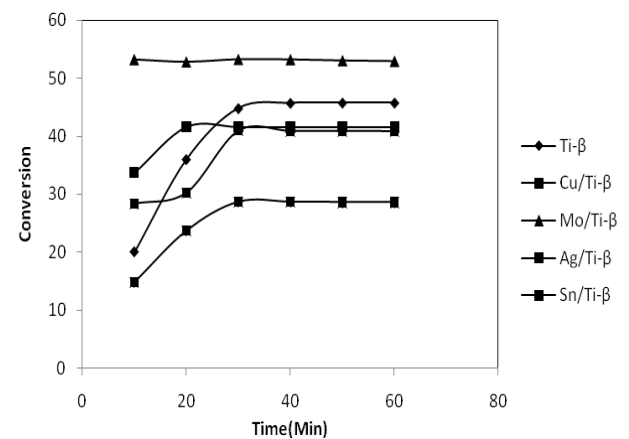


Fig 8: conversion of DBT with 4% metal impregnated Ti-β

Conversion of BT and DBT with Mo, Cu, Sn & Ag impregnated Ti-β catalysts was observed. It is observed that for treatment of BT highest conversion is achieved with 2.5% Sn/Ti-β and for treatment of DBT highest conversion is achieved with 2.5% Cu/Ti-β.

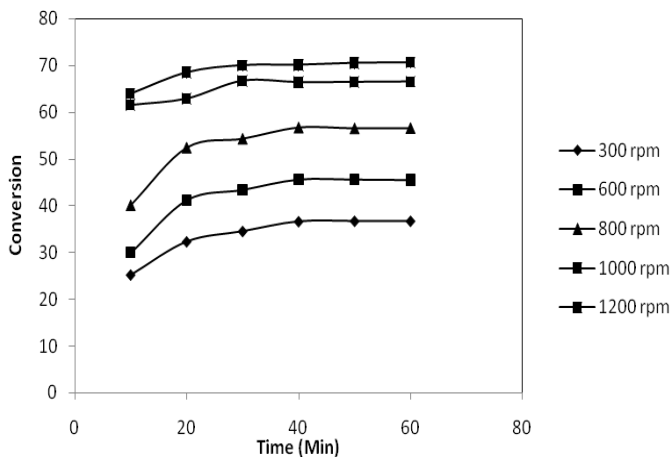


Fig 9: conversion of BT with stirrer speed

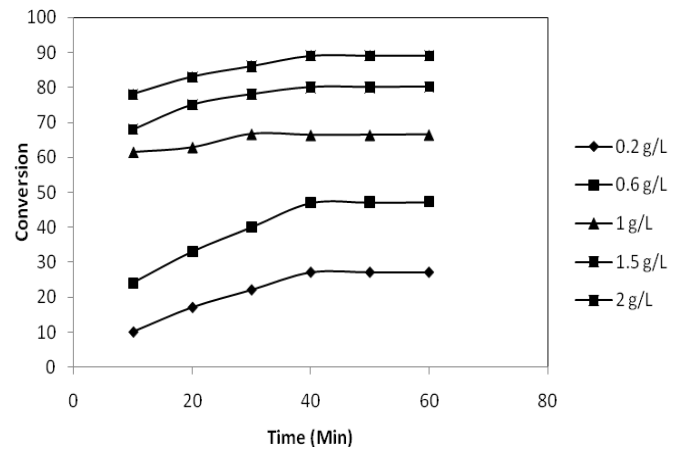


Fig 12: conversion of BT with catalyst concentration

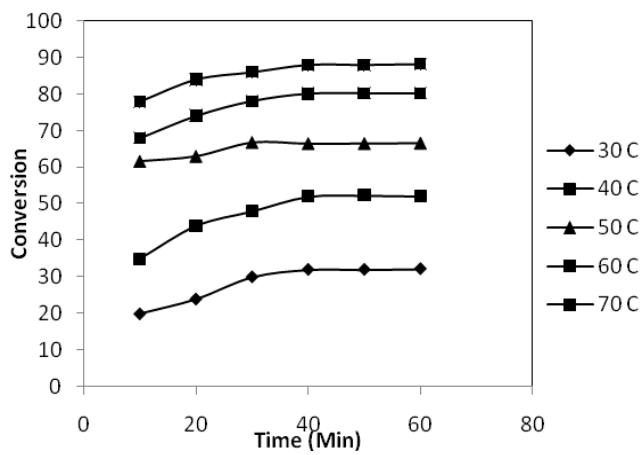


Fig 10: conversion of BT with temperature

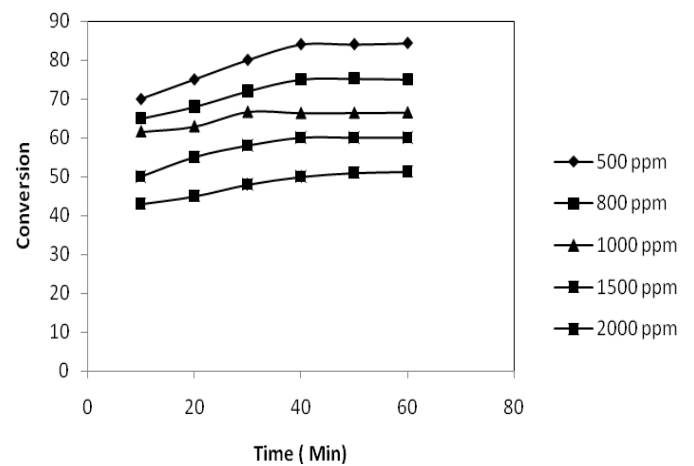


Fig 13: conversion of BT with sulphur concentration

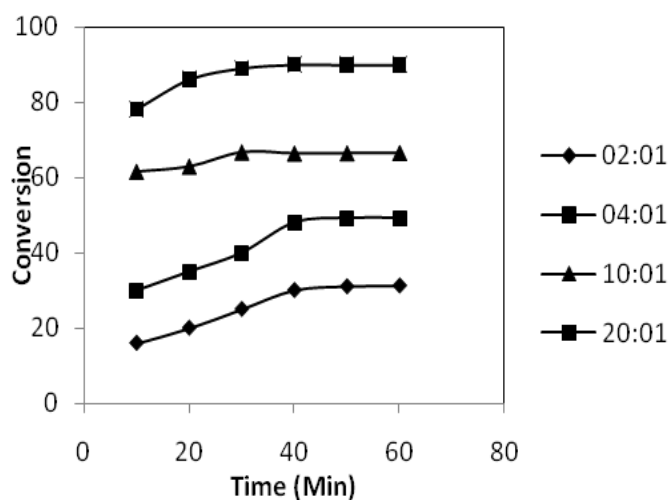


Fig 11: conversion of BT with TBHP:S ratio

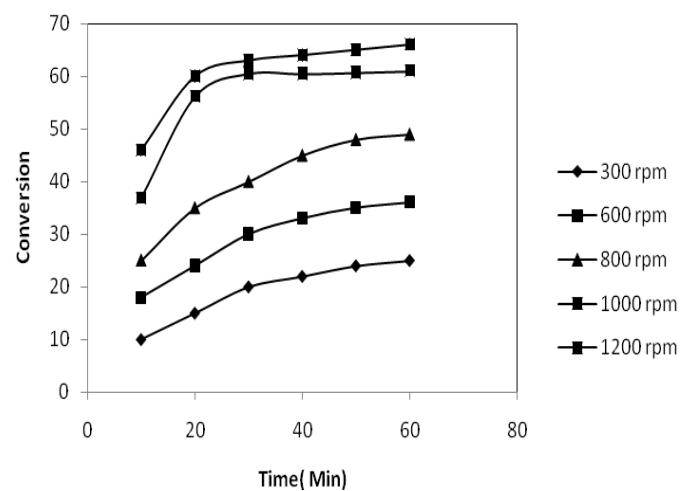


Fig 14: conversion of DBT with stirrer speed

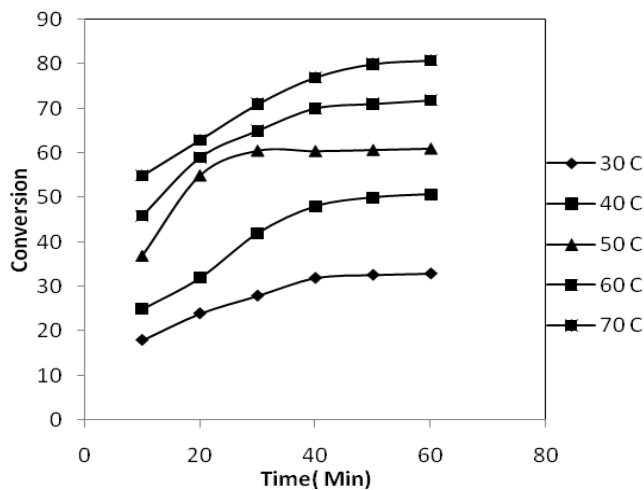


Fig 15: conversion of DBT with temperature

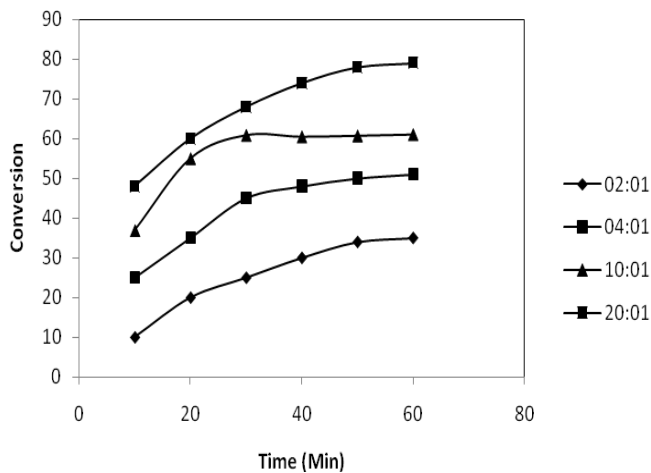


Fig 16: conversion of DBT with TBHP:S ratio

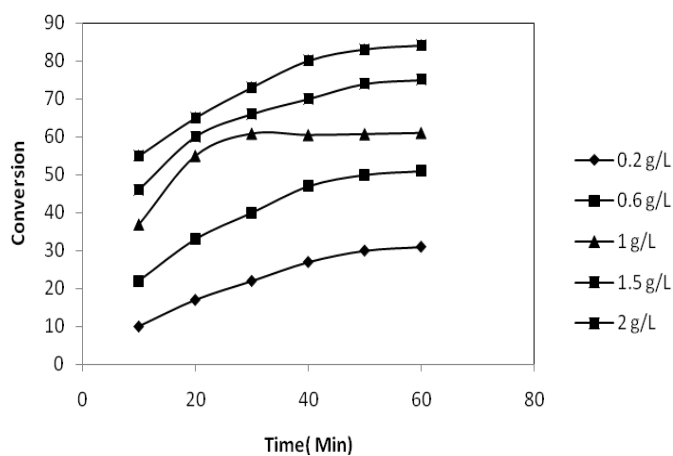


Fig 17: conversion of DBT with catalyst concentration

Conversion of BT and DBT is observed at stirrer speed of 300, 600, 800, 1000 and 1200 rpm. It is observed that conversion increases with stirrer speed and highest conversion is achieved for stirrer speed of 1200 rpm.

Conversion of BT and DBT is observed at temperature of 30°C, 40°C, 50°C, 60°C and 70°C. It is observed that conversion increases with temperature and highest conversion is achieved for temperature of 70°C.

Conversion of BT and DBT is observed at TBHP:S ratio of 2:1, 4:1, 10:1 and 20:1. It is observed that conversion increases with TBHP: S ratio and highest conversion is achieved for TBHP:S ratio of 20:1.

Conversion of BT and DBT is observed at catalyst concentration .2, .6, 1, 1.5 and 2 gm/l. It is observed that conversion increases with catalyst concentration and highest conversion is achieved for catalyst concentration of 2 gm/l.

Conversion of BT and DBT is observed at sulphur concentration of 500, 800, 1000, 1500 and 2000 ppm. It is observed that conversion decreases with sulphur concentration and highest conversion is achieved for sulphur concentration of 500 ppm.

Based on the above observations the optimum conditions were chosen as following:

Stirrer speed: 1200rpm

Temperature: 70C

TBHP: S ratio: 20:1

Catalyst concentration: 2gm/l

4. Conclusions

Conversion of BT and DBT with Ti-β as well as metal impregnated Ti-β was observed. Metal Loaded catalysts were found to deactivate after a certain time and conversion becomes constant. Best catalyst were chosen to be for BT 2.5% Sn/Ti-β and for DBT 2.5% Cu/ Ti-β. Parametric study was also conducted. Optimum reaction conditions are Stirrer speed: 1200rpm, Temperature: 70C, TBHP: S ratio: 20:1, Catalyst concentration: 2gm/l. It was also observed that we are getting highest conversion for 500 ppm sulphur concentration. Oxidation of BT and DBT was conducted using the best catalyst at optimum process conditions.

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