J. Environ. Nanotechnol.
Volume 2, No.3 pp. 25-28
ISSN (Print) : 2279-0748
ISSN (Online) : 2319-5541
doi : 10.13074/jent 2013.09.132028

Environmentally Friendly Synthesis of Ester of Acetic Acid by using Nanoporous $MgAlPO_4$ as Catalyst

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Received: 22.07.2013 Revised: 29.08.2013 Accecpted: 18.09.2013

Abstract

The liquid phase esterification of acetic acid with ethanol and n-butanol with no usage of mineral acid has been achieved by using recyclable and acidic nanoporous Mg substituted aluminophosphate ($MgAlPO_4$) as catalyst. The N_2 adsorption desorption measurements and electron diffraction patterns (SEM and TEM) makes a clear view about the nanopore and crystallinity of the catalyst $MgAlPO_4$. The optimization of experimental conditions for the esterification reaction like time, temperature, catalyst dosage, molar ratio of reactants and selectivity of the products were examined. The maximum ethanol conversion was found to be 87% and the selectivity of the product also very high.

Keywords: *$MgAlPO_4$; Esterification; Acetic acid; Ethanol.*

1. INTRODUCTION

Mostly mineral acids and metal containing lewis acid cataysts are used as catalysts for esterification reactions (Yijun Liu *et al.* 2006). These types of catalysts are very difficult to handle and creates environmental issues. In consideration of environmental issues, many efforts have been in progress to reduce the use of conventional acid catalysts by solid acid catalysts since these are easily recoverable, reusable and less harmful. Among the solid acid catalysts, metal substituted microporous and mesoporous aluminophosphates have attracted many researchers for its thermal stability and catalytic activity (Subrahmanyam *et al.* 2002; Subrahmanyam *et al.* 2003; Karthik *et al*. 2004; Masson *et al.* 2001; Joseph *et al*. 2004; Vijayasankar *et al.* 2010; Kannan *et al.*1998; Kannan *et al*. 1999; Cheralathan *et al*. 2000). Substitution of metal in the framework makes the material more suitable for acid catalyzed organic reactions. Eventhough, metal substituted $AlPO_4$'s have widely used in several organic reactions, only limited study has been made using these catalysts for esterification reactions (Zhao *et al.* 2001). Hence, in the present investigation, a newly synthesized thermally stable, nanoporous Mg substituted aluminophosphate molecular sieves (Devi *et al*. 2013) has been used as a catalyst in the liquid phase esterification of acetic acid with ethanol.

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2. EXPERIMENTAL

2.1 Synthesis

The synthesis of $MgAlPO_4$ was carried out by a simple method with the gel composition of $0.8Al_2O_3$:$1P_2O_5$:0.2MgO:0.5SDS:$300H_2O$ as per the prior report (Devi *et al.* 2013). The experimental set up for esterification reaction contains a batch reactor fitted with a reflux condenser and a thermometer. The alcohol-acid mixture was subjected to heating at various

temperatures with $MgAlPO_4$ catalyst. After the completion of the reaction, the reaction products were separated from solid $MgAlPO_4$ catalyst by filtration and the product was analyzed by gas chromatography (Chemito 1000 with FID detector). The effect of certain reaction conditions like temperature, contact time, catalyst dosage and molar ratio of the reactants were studied to optimise the maximum conversion of alcohol and product selectivity.

2.2 Characterisation

Scanning Electron Microscope (SEM) JEOL EO JSM-6390 was used for the determination of morphology of nanoporous $MgAlPO_4$. Transmission electron micrograph image (TEM) was recorded on a Philips 200 microscope operated at 160 kV.

3. RESULTS & DISCUSSION

3.1 Characterisation of $MgAlPO_4$

The characterization part of $MgAlPO_4$ was previously discussed in the literature by us (Devi *et al*. 2013). From the nitrogen adsorption desorption measurements, the pore size of the material was found to be 28.7 nm. This clearly reveals the presence of large nano pores in the material.

3.1.1. Electron diffraction studies

The morphology and textural properties of the calcined $MgAlPO_4$ was studied by SEM and TEM analysis. It is shown in Fig. 1 and Fig. 2. SEM image clearly represents the disordered morphology of the material with varied particle sizes in nano scale. The crystalline nature of the material was further confirmed by the TEM image Fig.2. The nano sized spherical particles proved the presence of crystallinity in the material. The white spots in the picture represent the disordered pore arrangement of the calcined $MgAlPO_4$. This difference in pore sizes in the range of 20 to 50 nm and the disorderness of the material might be due to the synthesis conditions.

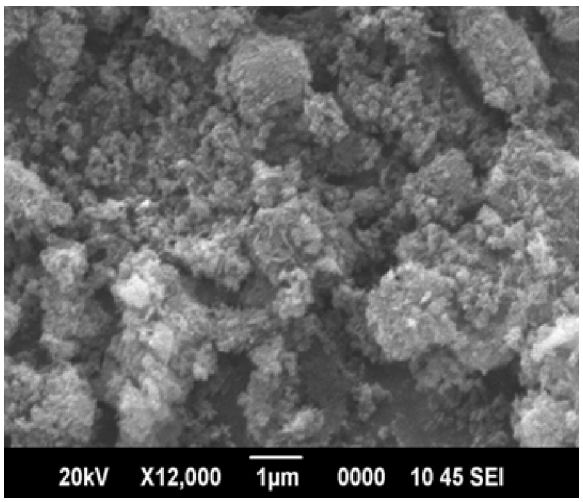

Fig. 1: SEM image of calcined $MgAlPO_4$

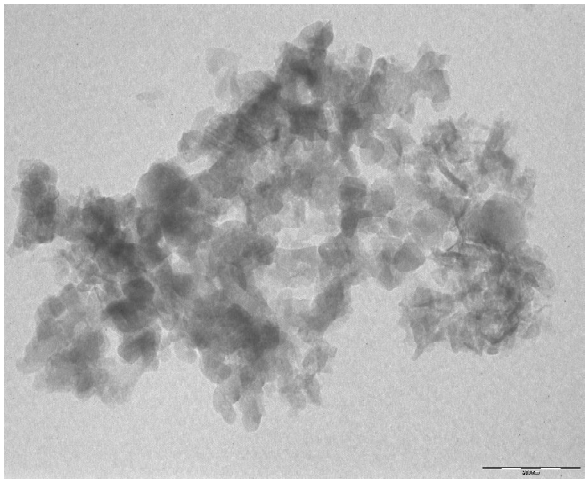

Fig. 2: TEM image of calcined $MgAlPO_4$

3.2. Esterification of acetic acid and ethanol

3.2.1. Effect of contact time

The reaction time taken for the esterification of acetic acid with ethanol over $MgAlPO_4$ was studied at 200 °C with the catalyst dosage of 0.5 g is shown in Table 1. The percentage of conversion of ethanol not

much considerably increases after 3h. The maximum conversion of 87% was achieved at 3h. The selectivity of ethyl acetate also remains high and almost similar. Hence, maximum contact time for the complete reaction is found to be as 3h.

Table. 1: Effect of reaction time on esterification of acetic acid over $MgAlPO_4$

Time (h)	Conversion of ethanol (%)	Product Selectivity(%)
		Ethyl acetate
1	75	98.9
3	87	99.3
5	86	99.7
7	87	99.4

Reaction conditions: acid:alcohol 3:1; Temperature 200 °C; Catalyst amount 0.5 g

3.2.2. Effect of reaction temperature

The optimisation of reaction temperature was investigated by altering the temperature from 50 to 200 °C with the acid : alcohol mole ratio of 3:1 for 3h. Fig.3 represents the conversion and selectivity of ethanol increased with the increase of temperature. It is found from the graph that at 50 °C, the ethanol conversion was very low. But at 100 °C and 150 °C, a tremendous increase in conversion was observed and almost remains same at 200 °C. Moreover, the selectivity of ethyl acetatealso stays constant. The activity of the catalyst increased with the increasing temperature. This makes the reaction feasible at high temperatures.

3.2.3. Effect of molar ratio of the reactants

The molar ratio effect of acetic acid with ethanol on esterification reaction was studied and shown in Fig.4. By increasing the acid to alcohol mole ratio from 1:1 to 5:1, a corresponding increase in the percentage of conversion was found up to 3:1 molar ratio. Increase in mole ratio after 3:1 diminished the percentage of

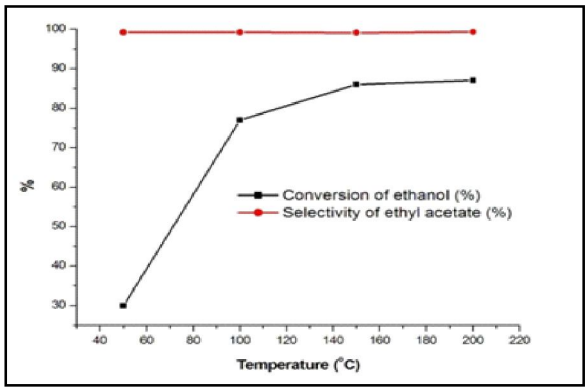

Fig. 3: Effect of temperature Vs conversion and product selectivity

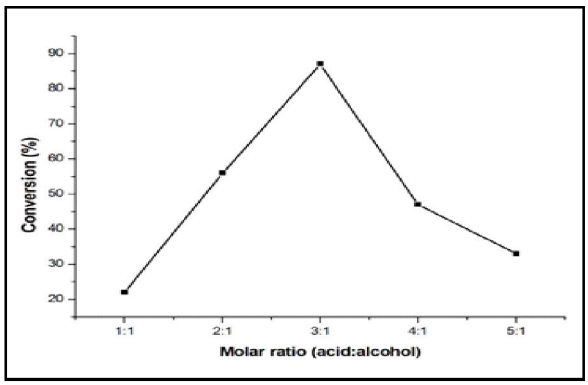

Fig. 4: Effect of Molar ratio Vs conversion

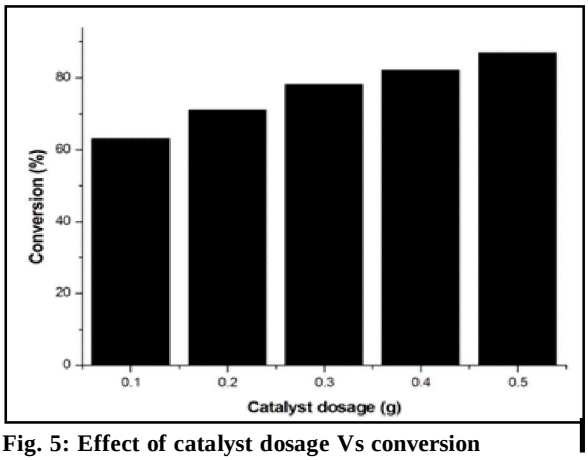

Fig. 5: Effect of catalyst dosage Vs conversion

conversion. The decrease in the conversion is due to the increase in the acid concentration which hides the active sites of the catalyst to react with alcohol.

3.2.4. Effect of catalyst dosage

The amount of catalyst for the esterification of acetic acid and ethanol was studiedby varying the catalyst dosage from 0.1 to 0.5 g. With the increase in the catalyst dosage, the conversion of ethanol also increases due to the increase in number of active sites in the catalyst. It is shown in Fig.5.

4. CONCLUSION

The industrially useful solvent ethyl acetate was successfully synthesized in an environmentally friendly atmosphere by using newly synthesized nanoporous $MgAlPO_4$ without using any added organic solvents and mineral acids. The optimisation of numerous experimental conditions like time, temperature, molar ratio of the reactants and catalyst dosage are studied and the maximum conversion of ethanol was found to be 87% and the product selectivity was also found to be high enough. Hence, this method of synthesis creates a non hazardous environment and generates high yield of products.

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