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Synthesis of Unusual Large Pore Mg Substituted Alumino Phosphate ($MgAlPO_4$) Mesoporous Molecular Sieve and its Catalytic Activity

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ABSTRACT

The substitution of aluminium by magnesium in the aluminophosphate framework ($MgAlPO_4$) by a simple synthesis using anionic sodium dodecyl sulphate(SDS) as surfactant leads to an active, selective and recyclable catalyst for the liquid and vapour phase polymerisation of styrene. The resulting material was characterized by means of FT-IR, BET surface area measurements, thermogravimetric analysis and temperature programmed desorption. With the aid of SDS, $MgAlPO_4$ material with the surface area and unusual large pore diameter of 52 m^2 g^{-1} and 28.7nm, respectively, were successfully developed in order to carry out large organic molecules transformation reactions. The TPD profile illustrates the presence of strong acid sites in the $MgAlPO_4$ frame work. Thus, it is found that mesoporous $MgAlPO_4$ acts as an active initiator and catalyst for the vapour phase polymerisation of styrene. The influence of temperature was examined for maximum conversion of styrene.

Keywords: Mesoporous magnesium aluminophosphate, Isomorphous substitution, Large pore diameter, Strong acid sites

INTRODUCTION

Variety of metal substituted micro porous aluminophosphates have been synthesized earlier and used as excellent catalysts for many organic reactions [1-11]. Incorporation of metal ions reveals a net negative charge to the neutral framework, which makes the material interesting for catalytic applications. However, the pore dimensions of these materials are not adequate to afford wide ranging organic molecules in their cavities. In order to overcome this problem, synthesis of mesoporous materials of increased pore dimensions has been in progress these days. Particularly, in the synthesis of mesoporous aluminophosphates, many strategies have been followed using different organic structure directing agents and synthetic conditions to enhance the catalytic activity of the materials [12-14].

In this view, metal substituted mesoporous aluminophosphates have attracted many researchers for its improved thermal stability and catalytic activity. Subramanian et al reported the oxidation of toluene over molecular oxygen using thermally stable Cr substituted mesoporous $AlPO_4$ and MCM-48 [15, 16]. According to Karthik et al, isomorphous substitution of Mg and Co into the framework of aluminophosphate makes the material highly acidic and they performed butylation of m-cresol over Mg and Co substituted mesoporous $AlPO_4$ and MCM-41 [17]. The thermally stable Mg substituted $AlPO_4$ with the maximum pore diameter of 4.4 to 6.6nm was obtained by N.C.Masson *et al* [18] using alkaline extraction of CTABr followed by calcination. Similarly, many metals like Mn, Zn, Fe [19, 20] have been reported to replace the Al^{3+} and/or P^{5+} in the structure of mesoporous $AlPO_4$. Almost, all the researchers followed the same synthetic routes (autoclave assisted hydrothermal synthesis) with distinct surfactants for the synthesis of mesoporous heteroatom substituted $AlPO_4$. However, no systematic study has been performed on the synthesis of heteroatom substituted mesoporous $AlPO_4$ using anionic surfactant (SDS) as template.

In the present report, we describe with one simple method for the synthesis of mesoporous Mg substituted $AlPO_4$ with large pore diameter (28.7nm) in the presence of anionic sodium dodecyl sulphate (SDS) surfactant as template. Due to the formation of large pore in the catalyst, a trial has been carried out in macromolecular reaction (polymerisation of styrene) using $MgAlPO_4$ as catalyst. Some of the polymers generally have commercial applications. Especially, the synthesis of polystyrene has gained much interest in the last decade especially in catalyst and polymerization research [21]. In recent years, polystyrene was synthesized by numerous synthetic procedures such as free radical, cationic and anionic, emulsion and homo polymerizations. In all the typical synthesis, catalyst, co-catalyst, initiator and solvents play a vital role which produces hazardous environment. In the present work, the polystyrene was synthesized only by the use of environmentally stable and non-hazardous $MgAlPO_4$ as catalyst.

MATERIALS AND METHODS

Chemicals: Aluminium hydroxide and magnesium chloride as aluminium and magnesium sources were purchased from Merck Ltd. Phosphoric acid and SDS were purchased from Loba chemie Ltd.

Catalyst synthesis: Mesoporous magnesium substituted aluminophosphate was prepared by using anionic surfactant SDS as template by a simple hydrothermal synthesis method with the following gel composition $1Al_2O_3:1P_2O_5:0.2MgO:0.5SDS:300H_2O$. To an aqueous solution of SDS, aluminium hydroxide was added under vigorous stirring. To this mixture, aqueous solution of phosphoric acid and magnesium chloride was added and stirring was continued for 2 h further in order to attain homogeneous mixture. The resulting gel was heated and dried at 150^oC in open air. The resulting solid was thoroughly washed with deionised water. The solid was then filtered, dried and calcined at 600^oC for 6 h to remove the organic template.

Characterisation techniques: Fourier transform infra red (FTIR) spectra of mesoporous AlPO4 was recorded in a Jasco FTIR-410 spectrophotometer in the range 4000–400 cm^{-1} using KBr pellet technique. Nitrogen adsorption–desorption measurements were made using a Micromeritics ASAP 2020 V3.00 H instruments, the sample was out gassed at 150^oC for 12 hrs. Thermogravimetry/differential thermal analysis (TG/DTA) measurements of the samples were made with thermal analyser (Perkin-Elmer Diamond TG/DTA) at a heating rate of 20^oC/min. Temperature programmed desorption (TPD) experiments were run under helium flow (50ml/min) and the amount of desorbed ammonia was measured by TCD detector. The TPD-NH_3 desorption curve was recorded at a rate of 5^oC/min from room temperature to 300^oC. The molecular weight of polymer was measured by gel permeation chromatography (GPC) equipped with two PL gel columns and calibrated over standard polystyrenes.

Catalytic reaction: Polymerisation of styrene was carried out over mesoporous $MgAlPO_4$ at various temperatures in a fixed bed vertical flow type reactor made of quartz tube with 40 cm length and 1.5 cm internal diameter was used. The quartz reactor was controlled by a digital temperature controller with an indicator. About 0.5g of mesoporous $MgAlPO_4$ was placed in the reactor and supported on either side with a thin layer of quartz wool. The reactant styrene was fed into the reactor through the peristaltic pump that can be operated at different flow rates. The bottom of the reactor was connected to a coiled condenser and a receiver in which the polymer was collected. The collected polymer with monomer was distilled to separate the polymer from the monomer and its molecular weight was determined by Gel permeation chromatographic technique.

RESULTS AND DISCUSSION

FT-IR spectral studies: The FT-IR spectra of asynthesized and calcined mesoporous $MgAlPO_4$ are shown in Fig. 1 (a and b). The Fig.1a shows the strong and broad band at 3,450 cm^{-1} which is assigned to the O–H vibration of water molecules that exists in the as-synthesized sample whereas in calcined magnesium substituted sample the strong O-H band becomes weak. The complete removal of the surfactant is confirmed by the characteristic C-H stretching bands at 2900 - 2800 cm^{-1} as well as C-H deformation bands around 1450 cm^{-1} are absent after calcination (Fig.1b) [13,22]. The strong band at 1130 cm^{-1} is ascribed to the symmetric stretching mode P–O of $PO_4{}^{3-}$ and the bending mode is positioned near 460cm^{-1}. Hence, it is confirmed from the spectra that there is no collapse in the tetrahedral framework of $MgAlPO_4$ after calcination.

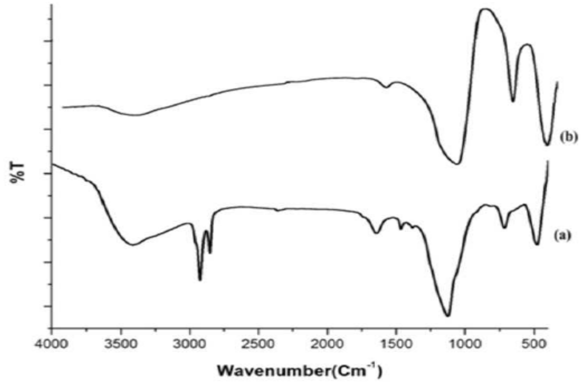


Fig.1: FTIR spectra of mesoporous $MgAlPO_4$ (a) asynthesized (b) calcined

Nitrogen adsorption–desorption measurement: Nitrogen adsorption–desorption isotherms of the calcined $MgAlPO_4$ are shown in Fig.2a. The observed well-defined inflection around $p/p_o = 0.5 – 0.9$, indicating that the mesoporous bodies are heterogeneously distributed [23] and it exhibits the type IV isotherm with a hysteresis characteristics of mesoporous material. The BET surface area and pore diameter of the $MgAlPO_4$ is found to be as 52m^2/g and 28.7 nm (Fig.2b). The enhancement in the pore diameter of the material was achieved by the new synthesis method and isomorphous substitution of Mg into the framework of $AlPO_4$. This is attributed to the Mg^{2+} cation which has larger radii than Al^{3+} [24,25].

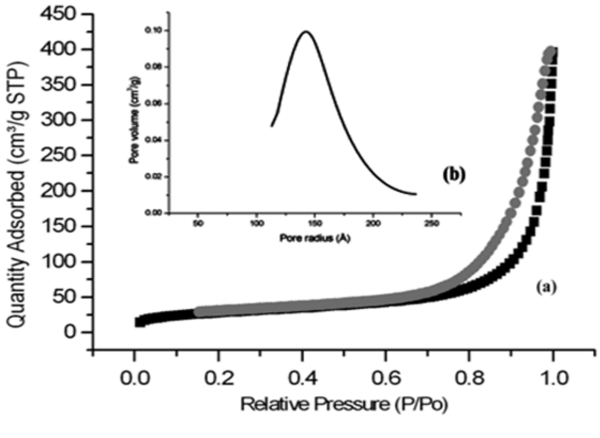


Fig.2: (a) N_2 adsorption – desorption isotherm of calcined $MgAlPO_4$
(b) Pore size distribution of mesoporous $MgAlPO_4$

Thermal studies: The TGA curve of $MgAlPO_4$ shows mainly three weight loss regions (Fig.3). The initial weight loss between 100 - 150°C is due to the loss of physisorbed water on the surface of the material. The corresponding second weight loss around 200°C may be attributed to the decomposition of the anionic template within the framework. The gradual final weight loss between 400 and 500°C is related to loss of water due to condensation of Mg-OH, P-OH, Al-OH groups in the framework [17].

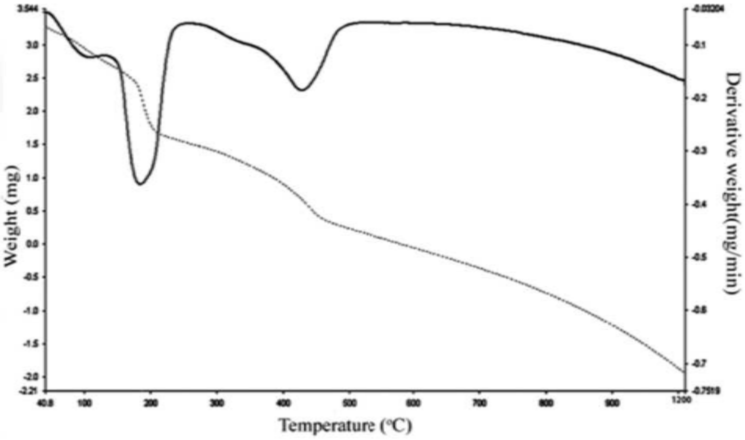


Fig. 3: TGA/DTA curve of assynthesized $MgAlPO_4$ molecular sieve

Temperature programmed desorption: The acidity of $MgAlPO_4$ sample was investigated by temperature-programmed ammonia desorption experiment (NH_3-TPD). The information on the acid strength distribution in $MgAlPO_4$ system can be obtained from TPD spectra. In the TPD curve of mesoporous $MgAlPO_4$ (Fig.4), the desorption of ammonia distributes at two different types of temperature. The desorption at 150°C to 170°C reveals the presence of medium acid sites (Lewis acid sites) and another desorption around 350°C proved the presence of strong acid sites due to the substitution of Mg in the framework of $AlPO_4$ system [15,17].

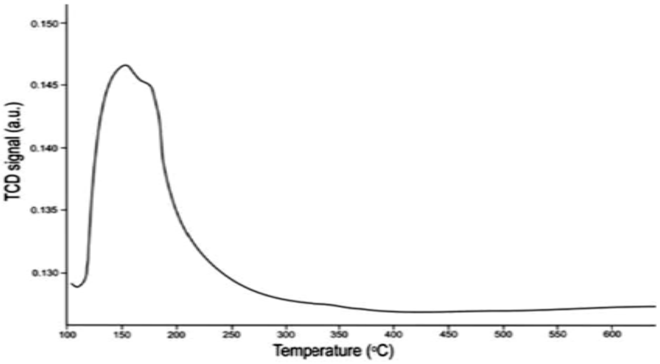
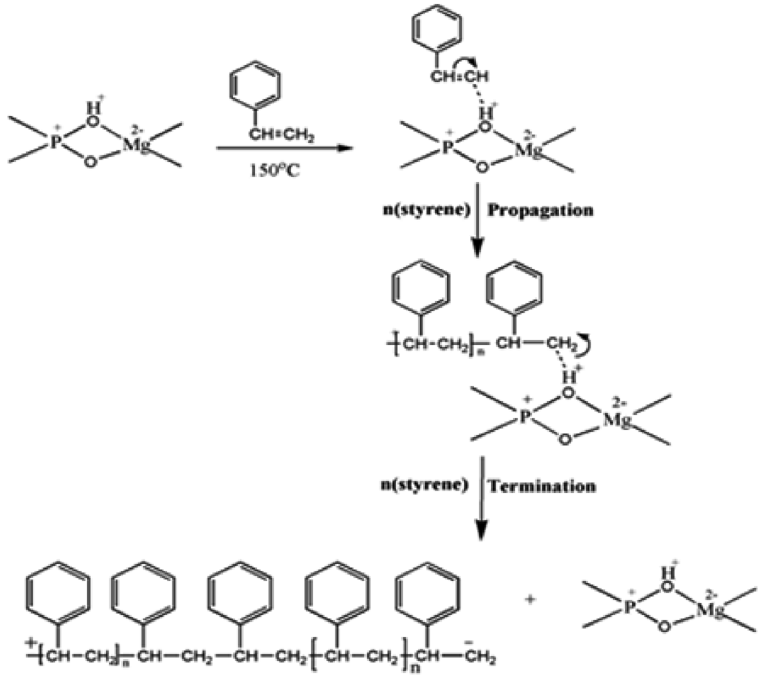


Fig. 4: Temperature programmed desorption (NH_3-TPD) of calcined $MgAlPO_4$

Polymerization of styrene over $MgAlPO_4$ catalyst: The acidic properties of the mesoporous $MgAlPO_4$ was confirmed by the polymerisation of styrene in vapour phase. The schematic representation of polymerization of styrene over $MgAlPO_4$ is shown in Scheme. 1. This markedly illustrates the initiation, propagation and termination of the reaction. In the initiation step of the polymerization of styrene, the Bronsted acid site of the catalyst initiates the reaction and the carbonation on styrene molecule propagates the polymerization.



Scheme.1: Mechanism of polymerisation of styrene over $MgAlPO_4$ catalyst

The polymerization of styrene over calcined mesoporous $MgAlPO_4$ as catalyst at various temperatures (50° to 250°C) was carried out without the use of any solvents. The percentages of conversion of styrene at various temperatures are shown in table 1.

Table 1. Percentage of conversion of styrene in liquid and vapour phase

Phase of reaction	Temperature(°C)	Flow rate of	Percentage of
	Styrene (ml/h)	conversion (%)	
Liquid phase	50	10	40
	75	10	54
	100	10	62
Vapour phase	150	10	92.2
	200	10	73.5
	250	10	69

($AlPO_4$ dosage: 0.5g)

From the table1, it is found to be clear that at low temperatures 50°C, 75°C and 100°C (i.e.) in liquid phase, the rate of polymerization was very slow, since the catalyst $MgAlPO_4$ was not fully activated at lower temperature. At 150°C (i.e.) in vapour phase, the higher conversion of styrene was observed. The number average molecular weight (Mn) of polystyrene was found as 20,180. Further increase of temperature up to 250°C not much influences the polymerization reaction. The decrease in conversion was due to the high velocity of styrene molecules crossed through the catalytic bed without any interaction with the active sites of the catalyst at higher temperatures. From this observation, the optimum temperature to carry out the polymerization of styrene over mesoporous $MgAlPO_4$ was found as 150°C. After the completion of the reaction, the catalyst can be reused by calcined the catalyst at 600°C.

APPLICATIONS

Thermally stable, large pore and highly acidic $MgAlPO_4$ can be utilized as a catalyst for the macromolecular organic reactions. The large pore in the catalyst provides enough space for the macromolecular reaction to proceed and also, the active acid sites of the catalyst initiates the polymerisation reaction as well. This environmentally benign synthesis of polymers without the use of any solvents establishes a new avenue in the field of catalysis.

CONCLUSIONS

Highly efficient heterogeneous, recyclable mesoporous $MgAlPO_4$ molecular sieve with enhanced pore size was successfully synthesized using SDS surfactant as template by a simple method. The TGA/DTA and BET measurements revealed the isomorphous substitution of metal Mg in the $AlPO_4$ framework. This approach is an easy and effective way to obtain high quality mesoporous $MgAlPO_4$ materials, and may be extended to the preparation of other kinds of mesoporous materials. The catalyst activity was attributed to its surface acid sites (Lewis acid and Bronsted acid sites) and mesoporous nature that allowed the macromolecular reaction (styrene polymerisation) to be completed at 150^oC with high yield.

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