Synthesis and Characterization of SAPOs Nanomaterial from Aqueous and Non-aqueous Media

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Abstract: Silicoaluminophosphate (SAPOs) molecular sieves were synthesized from aqueous and non-aqueous media. Effect of crystallization temperature for aqueous media and crystallization time for non-aqueous media were investigated. The synthesized samples were characterized by Powder-XRD, FTIR, and SEM. SAPOs nanomaterial was obtained at 150^0 C crystallization temperature for aqueous media. For non-aqueous media, the crystallization time was noticed 72 h for successive crystallization of SAPOs. It is observed that crystal size of SAPOs for non-aqueous media is smaller than aqueous media for it.

Keywords: Silicoaluminophosphate,non-aquoues media, SAPO 11, Nano-Crystalline materia, highly thermal resist mesoporous material.

1 INTRODUCTION

First time, nanocrystalline Silicoaluminophosphate (SAPOs) molecular sieves had been generated considerable interest as heterogeneous acid catalyst after synthesis of AlPOs in Union Carbide laboratories by Lok B.M. et al. 1982 [1]. In silicoaluminophasphate, the incorporation of silica atoms with alumina and phosphate atoms expose the distribution of hydroxyl group, acidic nature and acidic sites. Higher Bronsted acid sites generated by replacement of Al and P atom by silica called SM3 substitution which have responsible for the higher catalytic activity of SAPOs such as long chain hydrocarbon-isomerization and other acid catalytic reactions especially in petroleum refineries [2]. Among the pore structure with AEL framework was found most suitable for obtain high various SAPOs, SAPO-11 is elliptical 10-membered pore ring of 0.39 x 0.63nm, medium size unidirectional yield isomerisation of long-chain *n*-alkanes [3-5]. Si incorporation and Si dispersion was observedhigher in non-aqueous media than aqueous media during synthesis of SAPO molecular sieve. Due to higher Si incorporation SAPOs synthesized from non-aqueous media will possess larger surface area and smaller crystal size[6]. In present work, micro-porous molecular sieves Silicoaluminosilicates SAPO-11, was synthesized in aqueous and non-aqueous medium by Di-n-propylamine as structure directing agent and fumed silica as unique silica source.

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2 EXPERIMENTAL SECTION

2.1 Materials

Aluminium-Isopropoxide (98%, Spectrochem), Fumed-Silica (Aldrich), Orthophosphoric acid (85%, Merck), Ethylene Glycol (98 %, Merck), Di-n-Propylamine (98%, Spectochem), Double Distillation water.

2.2 Synthesis of Sapo-11.

In the typical synthesis of hierarchical SAPO-11 from aqueous and non-aqueous medium, proper amount of Aluminiumisopropoxide (AIP) was dispersed in distilled water and Ethylene glycol for aqueous and

non-aqueous media, respectively. This mixture was kept under constant magnetic stirring for 1h. Then, ortho-phosphoric acid was added dropwise and stirred continued for another 2h. Di-n-propylamine was added dropwise to the mixture as structure directing agent and stirrer continuous for 2h. Finally, fumed silica was added into the gel and stirred overnight for the complete mixing of gel. After that this gel is charged into the Teflon lined stainless steel autoclave. Crystallization was carried out at temperature range 120^{0}C to 180^{0}C and time from 24h to 72h. The product were washed well with distilled water and dried at 373 K and subjected to physiochemical characterization. The molar composition of synthesis gel was: 1.0AIP:6.3H_3PO_4:0.35SiO_2:0.6DPA:24M where M = H_2O (for aqueous) and M = EG (for non-aqueous). The synthesis conditions for the preparation of the SAPOs are given in Table 1.

TABLE 1

SAPOs synthesis with various temperature and time

Sample Run	Sample media	Temp °C	Time h	Relative Crystallinity
1	Aqueous	120	24	Amorphous
2	Aqueous	150	24	70%(AEL structure)
3	Aqueous	180	24	Amorphous
4	Non-aqueous	150	24	Amorphous
5	Non-aqueous	150	72	90%(AEL structure)

3 CHARACTERIZATION:

FTIR spectra of synthesized samples were recorded on Bruker Alfa Eco-ATR Germany, in the range of 600 to 4000 cm^{-1}. Powder X-ray Diffraction (PXRD) patterns of synthesized samples were recorded on Panalytic Instrument (Model Empyream XRD, Cu-Kα radiation, Ni - filter, Time/step = 0.0136s) in the 2Θ=5-90. Crystal size of synthesized samples was calculated by Scherrer equation. The surface morphology of the hydrothermally synthesized sample in aqueous and non-aqueous process was characterized by Scanning Electron Microscopy.

4 RESULT AND DISCUSSIONS

4.1 FTIR Analysis: IR spectra (Fig.1) studied for nature of hydroxyl group and incorporation of Silica. Asymmetric and Symmetric stretching vibrational frequencies for AlO_6 and PO_4 in range 600-400cm^{-1} and 900-1200cm^{-1} assign respectively. The band around 3600 cm^{-1} is predictable to the Bronsted acid sites o the [Si (OH) Al]. High frequency absorption band around 3660 cm^{-1} for SAPO 11 is belonged to the bridging Si-OH-Al hydroxyl group in the 12 ring channels. Small channels form due to low frequency absorption subsequent to hydroxyl group to framework. However higher frequency absorption of hydroxyl group shows relatively spacious channels[7].

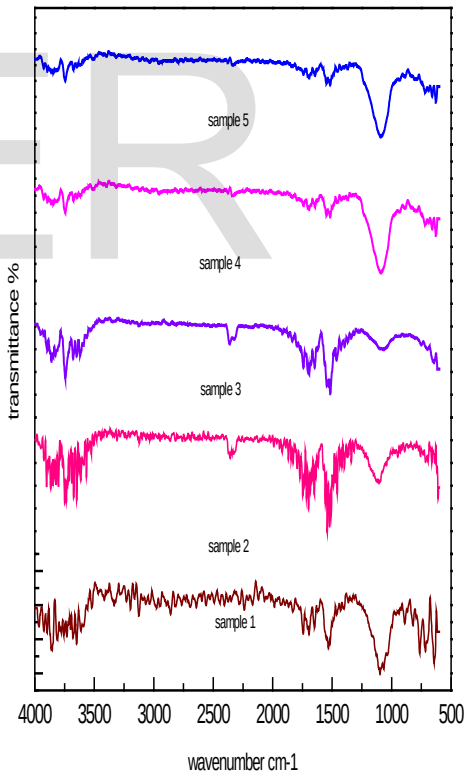

Fig.1 FTIR spectra of synthesized SAPO 11

4.2 PXRD Result. The PXRD pattern (Fig.1) shows that sharp peaks observed in sample 2 and sample 5 posses the AEL crystal structure and sample 1, sample 3 and sample 4 showed amorphous phase. From XRD pattern of sample 2 and 5, it was confirmed that

synthesized materials of sample 2 and 5 are SAPO-11 is only. Higher intensity of XRD lines indicates higher crystallinity for sample 2 and 5. It is verified that synthesis was carried out in using relatively low amount of DPA has given very attractive crystallinity of samples as compare to high contain DPA used. The XRD line broadening showed in sample 2 and 5 which indicates that very small crystals exist in both aqueous and non-aqueous media[8]. The relative crystallinity of sample 5 (Non-aq. media) was observed higher than sample 2 (Aq. media). Crystal size of sample 5 and sample 2 was calculated as 23 nm and 80 nm respectively. It was observed due to Si incorporation and Si dispersion may be higher in non-aqueous media than aqueous media during synthesis[6].

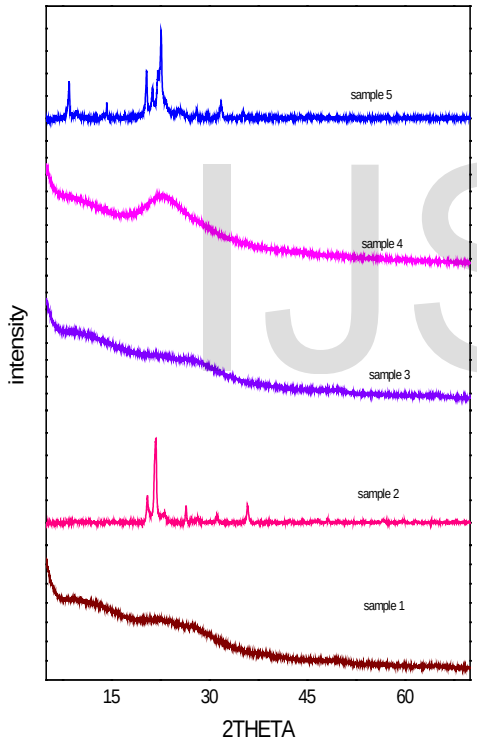

Fig.2 PXRD pattern of synthesized SAPO11

4.3 Surface Morphology SEM: The surface morphology sample synthesized in aqueous and non-aqueous media by hydrothermal method was characterized by Scanning Electron Microscopy. As shown in figure 1 (c) and (e) different crystal morphology was observer with 20-50nm crystal size. SEM micrographs fig. 1 (c) and (e) have shown pseudo- orthorhombic aggregates of nano-sized (20-50nm) crystals. Higher crystallanity observed at lower temperature (150^{0}c) for aqueous and non- aqueous media samples.

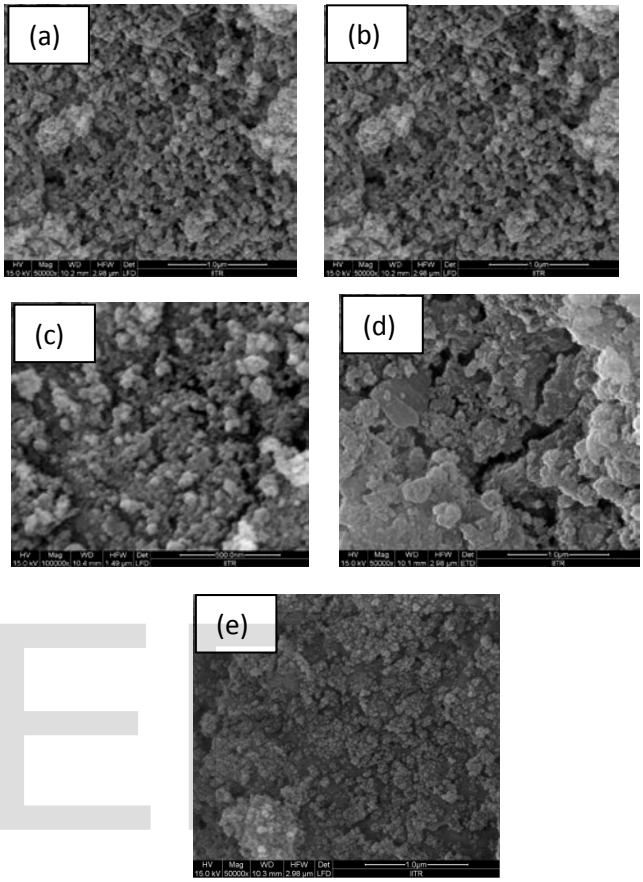

Fig: SEM micrographs of (a), (b) and (c) aqueous and (d), (f) non-aqueous SAPOs

5 CONCLUSION

SAPO-11 molecular sieve were synthesized successfully by aqueous and non-aqueous medium by Di-n-propylamine through the hydrothermal treatment method. The results confirmed that the sample had prepared successfully SAPO-11. The relative crystallinity of SAPOs synthesized in aqueous and non-aqueous medium differs due to change in crystallization temperature and crystallization time. Non-aqueous media sample observed higher crystallinity as well as smaller crystal size than aqueous media.

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