Research Inventy: International Journal of Engineering And Science
Issn (e): 2278-4721, Issn (p):2319-6483, PP: 13-18
www.researchinventy.com

Spectroscopic investigation of titanium sites in titanium containingnanoporous aluminophosphates-TAPO-5

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Abstract
Aluminophosphate molecular sieves commonly abbreviated as AlPO-n form a class of microporous crystalline materials having pore size in molecular dimension. Among the members of this family, AlPO-5 has been proven to be excellent heterogeneous catalyst in several organic transformations [1]. Si, Co, Zn, Mn, Mg, Cr, Ti and V metal ions. have been attempted into the framework of the aluminophosphate in order to modulate their catalytic properties. In principle, titanium can be stabilized in a aluminophosphate framework to yield a heterogenous oxidation catalyst. The present study is related to incorporation of titanium into a AlPO-5. The nature of sample, oxidation state of titanium, their location and stability have been studied by XRD, FT- IR, DRUV-Vis, TG-DTA, EPR, N_2 adsorption-desorption, FESEM and TEM techniques. Well crystalline titanium modified aluminophosphate structures were obtained. The samples were found to be highly porous (pore dimension ~ 5-8 Å) and of uniform shape.

I. Introduction

Aluminophosphates are novel type of molecular sieves, based on aluminium and phosphate, commonly termed as AlPO-n [1, 2]. Different atoms incorporated into the framework of AlPO-n to yield the modified metaloaluminophosphate (MeAPO) to make them catalytically active. Metalloaluminophosphates are microporous molecular sieves which is used for adsorption, ion exchange and catalytic reactions. Among the metaloaluminophosphates (MeAPO), titanium containing aluminophosphates (TAPOs) represents one of the most proficient oxidation catalytic systems. In particular, titanium containing molecular sieves are of interesting materials due to their unique catalytic behavior [3]. TAPO-n molecular sieves can have both ion exchange capacity and oxidative catalytic ability. Titanium containing molecular sieves called titanium aluminophosphate (TAPO-n) is also an interesting group where titanium is substituted into the frameworks of titanium aluminophospate (AlPO-n). Aluminophosphates building up a three dimensional framework [1, 2] consist of tetrahedral of Al(III) and P(V). Among the members of this family, AlPO-5 with its three dimensional pore systems has proven to be as a heterogeneous catalyst, which exhibits superior catalytic performances in several organic transformations [3]. Attempts have been made to incorporate Si, Co, Zn, Mn, Mg, Cr, Ti and V etc into the framework of the aluminophosphate in order to modulate their catalytic properties [4,5]. The catalyst is also non-selective towards the products. But this catalyst plays a significant role in Ti(IV) containing zeolite and/or zeolite-like molecular sieve catalysts are promising for certain oxidation reactions [6, 7]. Here with we report the characterization of titanium containing aluminophosphate-5 represented as TAPO-5 [8]. TAPO-5 phases have been repo alkylation, isomerisation and reforming [9]. TAPO-5 has been reported to be good and shape selective catalysts for oxidation reactions and offer several advantages such as easy separation and disposal [9].
The present study relates to the hydrothermal synthesis and systematic characterization of TAPO-5. TAPO-5 samples were characterized by various analytical and spectroscopic techniques.

II. ExperimentalSynthesis

Microporous TAPO-5 was synthesized by hydrothermal method with the gel composition; $1Al_2O_3$: 1.0 P_2O_5: 1.0 TEA : 0.01 Ti : 40 H_2O.

III. CharacterizationResults and Discussion

The as-synthesized and calcined samples were systematically characterized to study XRD, TGA, BET surface area, FT-IR, DRUV-VIS, FESEM, EDAX and TEM to study the formation of material as well as understanding the location, coordination and oxidation state of titanium .

3.1 Powder X-ray diffraction

The structures of the as-synthesized and calcined TAPO-5 were investigated by XRD shown in Fig.1. The XRD patterns of as-synthesized and calcined TAPO-5 were compared. The XRD patterns of both as-synthesized and calcined TAPO-5 showed several strong and weak reflections. After the insertion of titanium both AlPO-5 and TAPO-5 yielded similar reflection patterns which refer that AFI structure is retained . The incorporation of thetitanium into the AlPO-5 structure does not alter the ordered AFI structure.

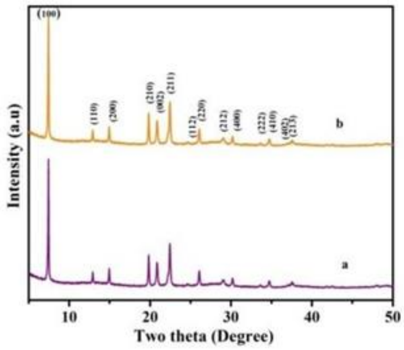


Fig.1: XRD pattern of TAPO-5: (a) as-synthesized (b) calcined.

3.2 Thermogravimetric Analysis

The thermal degradation behaviour of as-synthesized TAPO-5 material is illustrated in Fig. 2. It is noticed that TAPO-5 is a very stable material. About 22 % of total weight loss was noticed in thermogravimetry pattern of TAPO-5 which indicates the porous nature of material. In case of TAPO-5, 10% weight loss occurred below 393 K in the initial step due to desorption of physically adsorbed water molecule. About 7% weight loss occurred between 383-573 K in the second step corresponded to decomposition of template and in the third step 5% weight loss occurred in between 601-749 K is ascribed to the combustion of template molecules occludedwithin the channels of AlPO-5.

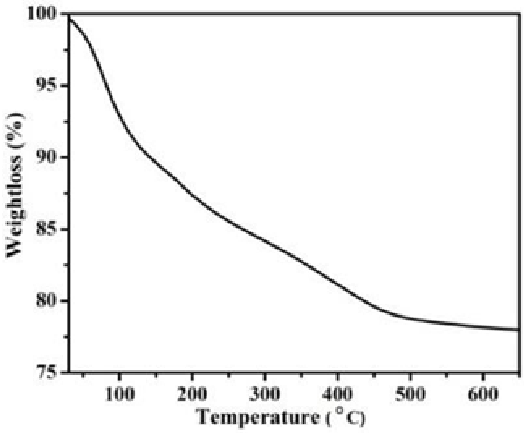


Fig. 2: TGA plot of as-synthesized TAPO-5.

3.3 Nitrogen adsorption-desorption Studies

The N_2 adsorption–desorption isotherm of TAPO-5 molecular sieve is shown in Fig.3. A broad and flat hysteresis observed between p/p_0= 0.7 to 1.0, typical characteristics of capillary condensation within meso-macropores, which is due to the pores those exist among intraparticle void space. Typical BET surface area measurement resulted in a value of 252 m^2g^{-1} for TAPO-5 which is an indicative of the microporous nature of TAPO-5. Pore volume was estimated to be 0.65 cm^3g^{-1}.

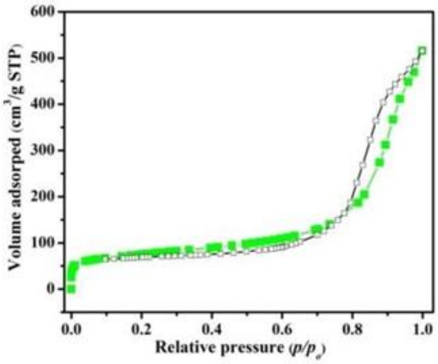


Fig. 3: N2 adsorption-desorption isotherm of calcined TAPO-5.

3.3 Fourier Transform Infrared Spectroscopy

FT-IR spectra of both as-synthesized and calcined TAPO-5 are shown in Fig. 4 and Fig.

5. A broad band, centered at 3452 cm^{-1} assigned to $-$OH stretching vibration region, refers to the surface hydroxyl group associated with P-/Al-/Ti-OH [10]. Weak absorption band at 1645 cm^{-1} is observed due to presence of adsorbed water and some oxidized carbonate phase [11]. All the aluminophosphates exhibited characteristics absorption peaks at 1100-1140 cm^{-1} range attributed to the asymmetric vibrations of phosphate. Occurrence of such feature can be attributed to the presence of abundant surface hydroxyl groups, making the surface hydrophilic.

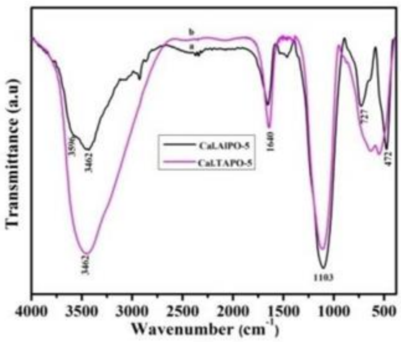


Fig. 4: FT-IR spectra of as-synthesized (a) AlPO-5 (b) TAPO-5

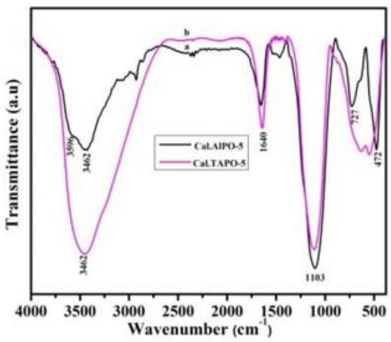


Fig. 5: FT-IR spectra of calcined: (a) AlPO-5 (b) TAPO-5

3.4 Diffuse Reflectance Ultraviolet Spectroscopy

The diffuse reflectance spectra were recorded for both as-synthesized and calcined TAPO-5 are shown in Fig. 6. The signal between 200-280 nm having λmax at 217 nm is attributed to Ti(IV) species in framework tetrahedral positions [12], i.e. characteristics of charge transfer transitions O→Ti(IV) involving tetrahedral Ti(IV) (scheme.1).

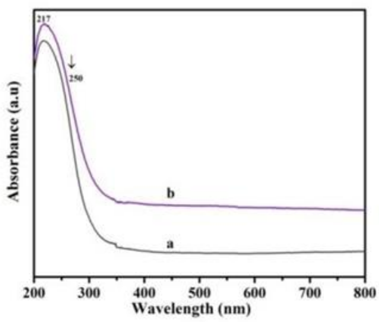
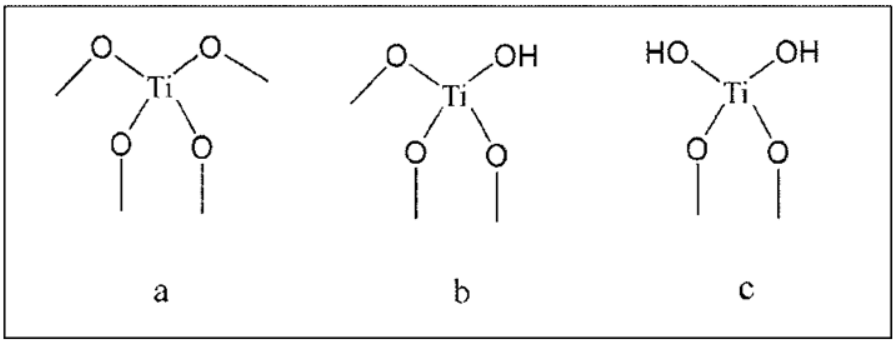


Fig. 6: DR UV-Vis absorption spectra of TAPO-5 (a) as-synthesized (b) calcined



Scheme. 1: Probable Ti(IV) sites in TAPO-5 [8].

An intense absorption band in the range 210-320 nm having band maxima at 250 nm is observed. The peak appeared at 250 nm is assigned due to the framework Ti(IV) as $Ti(OAl/P)_3OH$ (scheme.1b) or $Ti(OAl/P)_2(OH)_2$(scheme.1c). In calcined TAPO-5 the spectra show a similar absorption pattern that of the as-synthesized TAPO-5. It confirmed that Ti(IV) is retained in the tetrahedral framework after calcination. Broadening in the spectra is observed due to the distortion in tetrahedral symmetry. TAPO-5 do not contain anatase phase indicating the fact that titanium is incorporated in the microporous structure and/or remained in highly dispersed form.

3.5 Field Emission Scanning Electron microscope

In Fig.7 the field emission scanning electron microscopy (FESEM) images of the samples are shown. The morphology of TAPO-5 at different magnification along with EDAX containing elemental composition is summarized in Fig. 8. The pattern presented in figure (a) shows uniform and cuboid particles. The pictures also confirmed the phase purity [13]. Elemental composition of the sample was obtained from the EDAX analysis and it shows that sample contain Al, P, Ti and O (Fig. 8). The weight percent of elements are noted in the table obtained from EDAX . The elemental composition (in wt%) of TAPO-5 determined by EDAX analysis was Ti (0.30), Al (27.11), P (33.49), O (39.11).

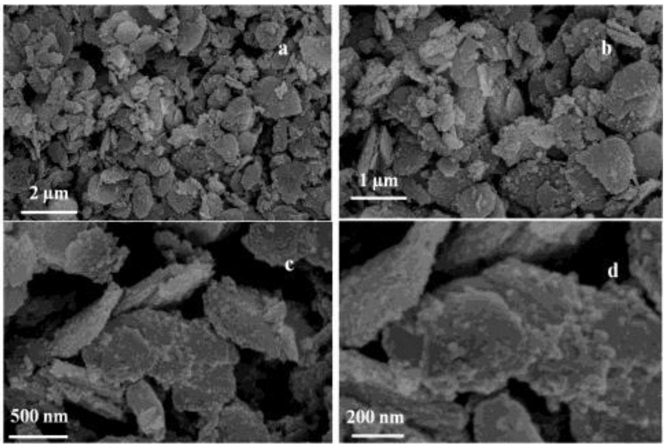


Fig. 7: FESEM of calcined TAPO-5

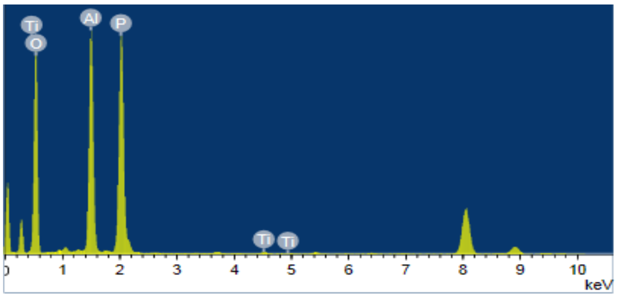


Fig. 8: EDAX of calcined TAPO-5

3.6 Transmission electron microscope

TEM images of TAPO-5 at different magnification are shown in Fig. 9. With the present resolution in the figure a porous network is distinctly seen [14]. The material possess thread like structures which are presumed to be assembled together to form flat sheet as clearly seen in fig. a, fig. b and fig. c which is in agreement with the SEM images. These thread like structures are having dimension less than 50 nm. Fig. 10 showed the pattern highly regular arrangement of lattice fringes.

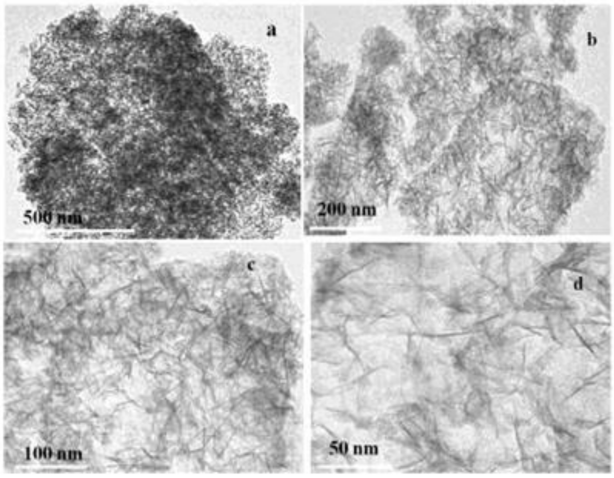


Fig. 9: TEM of calcined TAPO-5

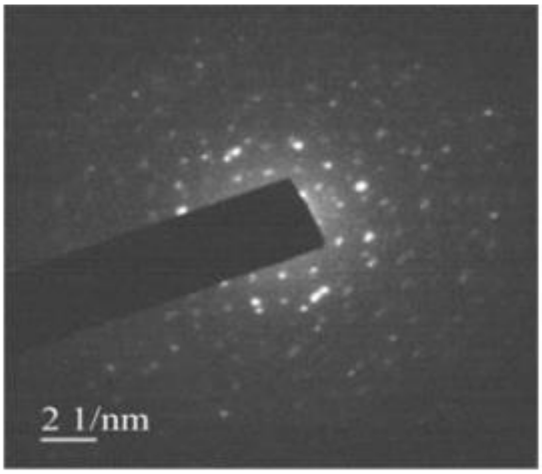


Fig. 10: SAED of calcined TAPO-5

IV. Conclusion

The formation of titanium containing aluminophosphate-5 (TAPO-5) is achieved through purity phase with good crystallinity. From thermal degradation behavior it is noticed that TAPO- 5 is a very stable material and hydrophilic. TAPO-5 predominantly occupies the tetrahedral sites as it is evident from electronic spectral studies and Ti(IV) is retained in the tetrahedral framework after calcination. Absence of any impurity such as anatase or rutile was also inferred from electronic spectral studies.TAPO-5 samples are observed flake like little surface roughness.

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