

Synthesis, Characterization and Catalytic properties of Vanadium Substituted Mesoporous Aluminophosphates

Ch. Subrahmanyam^a, B. Louis^b, B. Viswanathan^{a*}, A. Renken^b and T.K. Varadarajan^a

^aDepartment of Chemistry, Indian Institute of Technology Madras, Chennai-600 036, India.

^bInstitute of Chemical Engineering, Swiss Federal Institute of Technology, CH-1015 Lausanne, Switzerland.

Abstract : Vanadium substituted mesoporous AlPO has been synthesised using structure-directing surfactant under hydrothermal synthesis conditions. The presence of V in the framework of AlPO has been established by ESR, XPS, UV-VIS DRS and ICP-AES measurements. The synthesised system is capable of promoting the oxidation of toluene to aldehyde and benzoic acid when the oxidising agent is 70 % TBHP while with 30% H₂O₂ cresols are also formed. The activity of V-AlPO has been compared with those obtained with other similar porous materials like V-MCM 48, V-MCM-41, V-Al-Beta and VS-1

Keywords: V-AlPO, V-MCM-48, toluene oxidation, mesoporous materials, and *tert*.butyl hydroperoxide (TBHP)

1. Introduction

A significant break through in zeolite science occurred in 1982, when Wilson et al. [1] first reported the synthesis of new class of microporous crystalline aluminophosphate materials (AlPO₄). Later Flanigen et al. [2] reported the successful incorporation of 13 elements into the framework of AlPO-5. Though these materials are active for various shape selective oxidation reactions, their potential is restricted because of the number and type of heteroelements that can be incorporated into the framework is limited. The pore sizes of the resulting molecular sieves are also another factor for consideration.

Synthesis of molecular sieves by structure-directing effect of ordered aggregates of surfactant molecules [3] opens a path to obtain mesoporous

molecular sieves with controlled pore sizes and with various other elements. Various transition metal ions have been incorporated and the resulting systems are potential catalysts. However, much attention has not been paid to the synthesis of mesoporous aluminophosphates. Efforts to make hexagonal mesoporous aluminophosphates include a first brief report by Kimura et al [4]. Later the same group reported the formation of stable mesoporous AlPO's using surfactants with long alkyl chains [5, 6]. Feng et al reported the synthesis of mesoporous AlPO's at room temperature through fluoride route [7]. Hexagonal, cubic and lamellar aluminoborates were also prepared [8]. The mechanism involved in the formation of silica based M41S series for the incorporation of

* To whom correspondence should be addressed
E-mail: bviswanathan@hotmail.com, Tel: +91-44-257 8250.

silica in AlPO framework was investigated [9]. Incorporation of Si, Ti, V, Cr, Mn and Fe in mesoporous AlPO network has also been reported [10-17]. Recently, Ti-AlPO has been synthesised [12] and demonstrated as potential catalyst for oxidation of various organic substrates with 30% H₂O₂.

The present communication deals with the formation of V-analogues of mesoporous aluminophosphates via surfactant based hydrothermal synthesis. Their catalytic activity was tested for the partial oxidation of toluene with TBHP and H₂O₂ as oxidants and compared with that of V-MCM-48.

2. Experimental

2.1 Synthesis

Mesoporous vanadoaluminophosphates were prepared using CTAB as surfactant and with the following gel composition. 0.95Al₂O₃: 1 P₂O₅: 0.05V₂O₅: 0.4-0.5 CTAB: 300 H₂O. Various sources of aluminium have been tried and aluminium hydroxide has been chosen as the source. The pH of the gel was maintained at 9.5 with tetramethyl ammonium hydroxide, as the use of other sources like NaOH and NH₄OH led only to amorphous materials. The resulting gel was aged at room temperature for 3h followed by autoclaving at 423 K for 24h. The solid was filtered, washed several times with deionised water and calcined at 773 K for six hours to remove the organic template.

V-MCM-48 materials were synthesized under hydrothermal conditions at 423K in a static stainless-steel autoclave. In a typical synthesis of V-MCM-48, to a 25% aqueous solution of cetyltrimethylammonium bromide (CTAB) (S.D. Fine Chem.)

tetraethylorthosilicate (TEOS, 98%, Merck-Schuchardt) is added along with required amount of vanadium acetylacetonate (Fluka). The pH of the gel was adjusted to 10.0-10.5. The typical molar gel composition was SiO₂: V_xO_y: CTAB: Na₂O: EtOH: H₂O = 2.0: 0.015: 0.24: 0.5: 5.0: 195. The gel was stirred for 3h at room temperature and autoclaved at 423 K for 10 h. The solid product was filtered, washed several times with deionised water, dried in air at 373 K over night, calcined for 1h in N₂ atmosphere followed by heating in air at 823 K for 10h. Pure silica materials were also prepared by the same procedure. In general, extra framework cations will mainly contribute to homogeneous catalysis. In order to remove the extra-framework vanadium ions present in the mesoporous catalysts, the calcined materials were washed with ammonium acetate solution (1M) for 12h, filtered, dried at 373K and calcined at 773 K for 6h in air.

2.2 Characterisation

Various techniques have been used for the characterisation of the materials synthesised. The low angle X-ray diffraction pattern of the sample was recorded on a Siemens D 500 ($\theta/2\theta$) using monochromatised Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) with a scan speed of 1°/min over the range $2 < 2\theta < 10^\circ$. ICP-AES was done with Labtam Plasma Lab 8440. Thermal analysis of the samples was made with thermal analyser (Perkin Elmer model TGA 7) at a heating rate of 20 °C/min. diffuse reflectance UV-VIS DRS spectra were carried out on a Cary 5E UV-VIS-NIR spectrophotometer. ESR spectra were recorded with Varian E-112 spectrometer at liquid nitrogen temperature (77 K). N₂ adsorption-desorption at 77 K measurements were

made using a CE instruments, Sorptomatic 1990. The sample was out gassed at 473 K for 12 h. X-ray photoelectron spectroscopic measurements (XPS) were performed on a PHI-550 ESCA-System (Perkin-Elmer GmbH). The V_{2p} region between 510-520eV was studied in detail.

2.3 Catalytic activity

Oxidation of toluene was carried out at 333K in a three necked round bottomed flask under reflux conditions using 70 % TBHP as oxidant. Acetone, acetonitrile and methanol were used as solvents. The temperature was maintained by a thermostated oil bath. After each experiment, XRD was recorded to examine the morphological changes. The reaction products were identified by GC-MS (Hewlett-Packard, HPG 1800A GCD system, HP-5) and analysed by gas chromatograph (Shimadzu GC-14A, 30m HP-5. FID).

3. Results and discussion

3.1 XRD measurements

The XRD pattern of V-AlPO materials is given in Fig. 1. The pattern has been indexed on the basis of hexagonal lattice characteristic of MCM-41 type structure. The as-synthesised material shows a maximum intense peak corresponding to (100) reflection followed by a broad peak corresponding to (110) and (200) reflections that can be indexed to a hexagonal lattice. After calcination, intensity of d_{100} slightly decreased in comparison with as-synthesized material, however the sample retained its hexagonal structure after calcination.

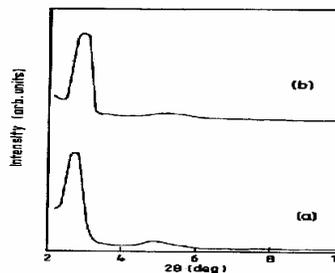


Fig. 1. XRD pattern of V-AlPO (a) uncalcined (b) calcined

An organic base, tetramethylammonium hydroxide (TMAOH), was used to maintain the pH of the gel. The function of organic ammonium cation from TMAOH is probably to modify the strength of the electrostatic interactions between the aluminophosphate species and the cationic surfactant micelle assembly to form the $S^+ I^- / TMA^+$ ion pair. If either NaOH or NH_4OH is used, the smaller cations Na^+ , NH_4^+ compete with the aluminophosphate species and thus restrict the interaction with the positively charged cationic surfactant [10]. As stated earlier, aluminium hydroxide may form a less polymerised aluminophosphate with many hydroxyl groups and favour the assembly of the mesostructure compared to other aluminium sources.

The powder X-ray diffractograms of as-synthesised and calcined V-MCM-48 samples are given in Fig. 2. It can be seen that highly ordered MCM-48 mesoporous materials consistent with an $Ia3d$ cubic symmetry were obtained. In the procedure adopted in the present study the synthesis of the MCM-48 at low surfactant to silicon

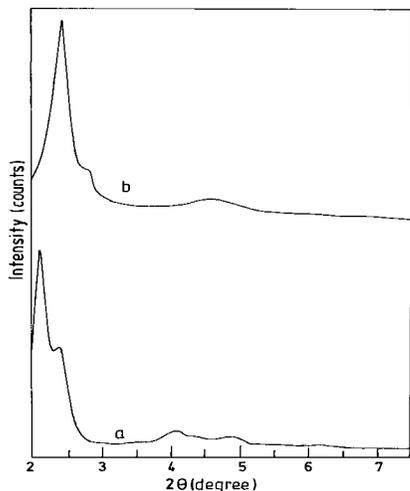


Figure 2. XRD patterns for V-MCM-48 materials a) Uncalcined b) Calcined

ratio was achieved, unlike the synthesis reported by Mobil researchers where higher ratios are mandatory to obtain the cubic structure [18]. The V-MCM-48 materials exhibit a maximum intense peak with d_{211} value of 35.30 Å, which on calcination decreased to 33.80 Å. In addition to reflection due to (211), these materials show less intense peaks corresponding to (220), (321), (400) and (322) reflections. After the calcination at 823 K in air, the cell parameter calculated was found to be 82.79 Å. After the catalytic experiments, the material shows similar XRD pattern indicating the material maintains the morphology even after the reaction.

3.2 Thermal analysis

The thermogram for AlPO samples (Fig. 3) in the temperature range 323-1073 K, shows mainly two weight loss regions and total weight loss corresponds to 40 %. This weight loss includes a first region at 353-393 K corresponding to the loss of physisorbed water. The second and main in the region 493-533 K corresponds to the removal of the template. It was observed that AlPO samples are stable

up to 1073 K unlike the stability reported up to 973 K [10].

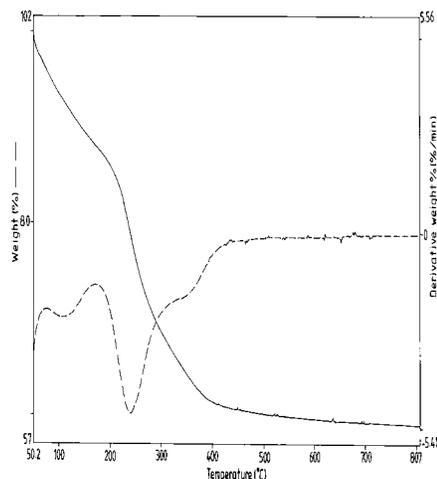


Figure 3. Thermogram for V-ALPO

3.3 N₂ adsorption

The N₂ adsorption-desorption isotherms for V-MCM-48 and V-ALPO materials are given in Fig. 4. MCM-48 materials show type IV adsorption-desorption isotherms with a hysteresis loop. The isotherms have an inflection around $p/p_0 = 0.2-0.3$ indicative of mesoporous nature. The surface area is $\sim 845\text{-m}^2/\text{g}$ and average pore size is 28 Å.

In the case of V-AlPO materials, N₂ adsorption isotherms also show typical hysteresis loop characteristic of mesoporous materials. The existence of small hysteresis indicates disorder in shape. BET surface area is 650 m²/g, with a pore size around 28 Å.

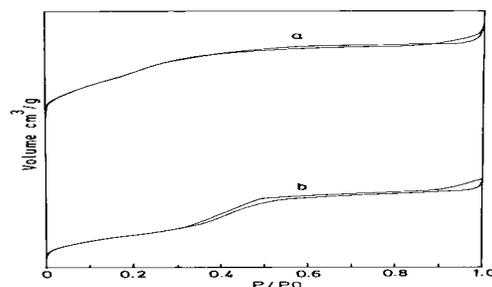


Figure 4. N₂ adsorption-desorption isotherms of a) V-MCM-48 b) V-ALPO

3.4 UV-VIS DRS

The UV-VIS DRS spectrum of the as-synthesised AIPO sample shows a band in the region 250-285 nm characteristic of V^{4+} charge transfer band of VO_2^+ species. However, in calcined sample (Fig. 5), the presence of an additional band between 285-340 nm confirms the presence of V^{5+} in T_d environment [19]. The similar features are also observed in the case of V-MCM-48.

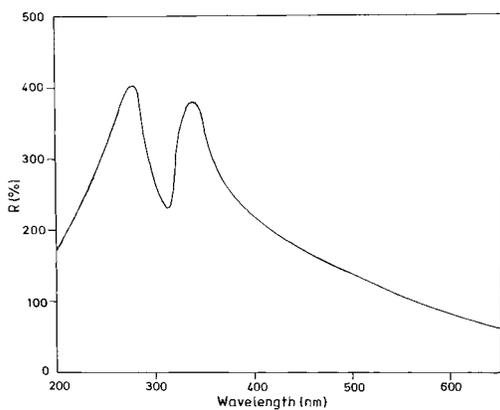


Figure 5. UV-Vis spectrum for V-ALPO

3.5 ESR spectroscopy

The ESR spectra of as-synthesised and calcined AIPO samples are given in Fig.6. It exhibits an axially symmetrical signal of tetravalent vanadium, which originated from the d^1 electron interaction with nuclear spin ($I_n = 7/2$) of ^{51}V . As-synthesised sample exhibits ESR signals. The EPR parameters ($g_{||} = 1.948$, $g_{\perp} = 1.99$, $A_{||} = 191$ G, $A_{\perp} = 70$ G) indicate that V^{4+} is present in a distorted O_h environment [19]. Upon calcination, the signal intensity decreased and sharpness of the signal was increased. This is due to partial conversion of V^{4+} to V^{5+} during calcination process. This supports the observation of a band in the region 285-340 nm in UV-VIS spectrum.

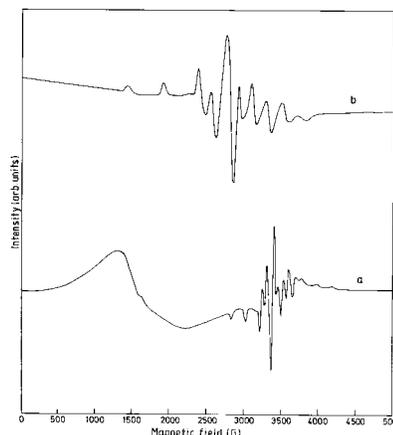


Figure 6. ESR spectrum of V-ALPO a) calcined b) uncalcined

3.6 XPS measurements

The XPS spectra of calcined V-ALPO in V_{2p} region (515-518 eV) shown in Fig.7 indicate two peaks: one corresponding to V^{4+} at 516 eV and other one corresponding to V^{5+} at 517.4 eV. This confirms our contention that during calcination partial oxidation of vanadium takes place. XPS in combination with UV-VIS DRS and ESR data confirm the presence both +4 and +5 oxidation states of vanadium.

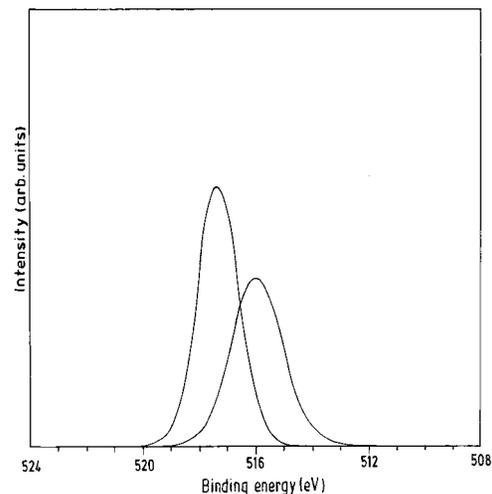


Figure 7. XPS spectrum for calcined V-ALPO (after deconvolution)

3.7. Catalytic activity

The presence of vanadium in the aluminophosphate framework has been

ascertained by various characterisation techniques. ICP-AES analysis of calcined V-AIPO shows 0.5 wt% of vanadium. The oxidation of toluene with 70 % TBHP as oxidising agent was carried out with V-AIPO and V-MCM 48 at 333 K in a variety of solvents and the results are summarised in Tables 1 and 2 respectively. The oxidation of toluene produced benzaldehyde, benzoic acid and benzyl alcohol with high selectivity towards aldehyde. Interestingly, under the reaction conditions employed for the oxidation of toluene with TBHP, it was observed that both V-AIPO as well as V-MCM-48 has not produced any detectable amount of cresols indicating that these catalysts are promising side chain oxidation catalysts. When the reaction was performed in the absence of solvent, conversion and selectivity are low. It was observed that acetone is better solvent for oxidation of

toluene with TBHP compared to other solvents like acetonitrile and methanol. This could be due to the solubility of toluene and TBHP in acetone. The stability of vanadium containing mesoporous aluminophosphate materials for liquid phase oxidation reactions with TBHP suggests that the aluminophosphate framework (Al^{+3} , $r = 0.053$ nm) can accommodate vanadium ($V^{+4/+5}$, $r = 0.059/0.046$ nm) centres in a better way than silicate framework (Si^{4+} , $r = 0.040$ nm) of MCM-48. In order to examine the catalytic activity due to leached metal ions, in a separate experiment, the reaction mixture was filtered after 2 h in hot condition and the experiment was continued with the filtrate. Increase in conversion was not observed, indicating homogeneous catalysis is not taking place under the reaction conditions.

Table 1. Catalytic activity of V-ALPO for toluene oxidation with 70% TBHP
Reaction conditions: Catalyst = 100mg, Substrate: TBHP: Solvent = 1 :2 :5
(mole ratio) T= 333 K, t= 6h

Solvent	Conversion (%)	Product selectivity (%)			
		Benzaldehyde	Benzoic acid	Benzyl alcohol	Others
None	8.5	78.5	16.5	2.0	3.0
Acetone	27.4	76.5	20.4	3.1	---
Acetonitrile	21.5	73.3	22.8	3.9	--
Methanol	14.3	39.0	26.1	6.3	28.6 ^a

Where a is Methyl benzoate

Table 2. Catalytic activity of V-MCM-48 for toluene oxidation with 70% TBHP
Reaction conditions: Catalyst = 100mg, Substrate: TBHP: Solvent = 1:2:5
(Mole ratio) T= 333 K, t= 6h

Solvent	Conversion (%)	Product selectivity (%)			
		Benzaldehyde	Benzoic acid	Benzyl alcohol	Others

None	5.5	71.4	20.0	5.1	3.5
Acetone	23.2	74.4	21.1	4.5	--
Acetonitrile	19.4	70.9	23.9	2.5	3.0
Methanol	11.2	34.4	24.0	10.5	31.1 ^a

Where a is Methyl benzoate

For comparison, the same reaction has been performed with 30 % H₂O₂ with acetonitrile as solvent and results are given in Table 3. V-AIPO is more active and selective to benzaldehyde over other V-substituted molecular sieves. Considerable quantity of cresols has been observed in all the cases. It was observed that V-MCM-48 shows a slightly higher conversion compared to V-MCM-41. This could be due to the interwoven network of cubic MCM-48 where the diffusional constraints are less compared to the one-dimensional hexagonal MCM-41 network. The higher activity of V-

substituted mesoporous materials suggests high dispersion of vanadium in mesoporous framework, which is a prerequisite for the oxidation reactions.

4. Conclusion

The incorporation of vanadium in the framework of aluminium phosphate materials has been achieved through structure directing template route. Vanadium (V⁴⁺/V⁵⁺) substituted AIPO's have been shown to be promising oxidising catalysts with 70 % TBHP and 30 % H₂O₂ as oxidising agents. V-AIPO showed higher activity as compared with that of other similar porous materials like V-MCM48 and V-MCM 41.

Table 3. Comparative activity of various catalysts for toluene oxidation with 30 % H₂O₂
Reaction conditions: Catalyst = 100mg, Toluene: 30 % H₂O₂: Acetonitrile = 3:1:10
T= 353 K, t= 24h

Catalyst	Conversion (%)	Product selectivity (%)					
		Benzaldehyde	Benzoic acid	Benzyl alcohol	O-Cresol	P-Cresol	Others
V-ALPO	28.4	64.4	4.1	4.0	12.0	9.8	1.0
V-MCM-48	22.7	67.2	6.0	1.5	15.5	10.5	4.0
V-MCM-41 ²⁰	20.8	62.0	--	2.0	20.0	14.0	2.0
V-Al-Beta ²¹	14.0	56.0	--	4.0	21.0	17.0	2.0
VS-1 ²²	11.7	52.2	--	7.7	19.7	17.1	3.7

Acknowledgements

The authors are grateful to Dr. Kiwi-Minsker for fruitful discussions and to Mr. N. Xanthopoulos and P. Möckli for kindly providing us the XPS and XRD data reported in this paper.

We are also thankful to RSIC, IIT-Bombay for ICP analysis.

References

- [1] S.T. Wilson, B. M. Lok, C. A. Messina, T. R. Cannan and E. M. Flanigen, J. Am. Chem. Soc. 104 (1982) 1176.

- [2] E.M. Flanigen, B.M. Lok, R.L. Patton, S.T. Wilson, in: Proceedings of the 7th International Zeolite Conference, Tokyo, Japan, 1986, p. 103.
- [3] T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli, J.S. Beck, *Nature* 359 (1992) 710.
- [4] T. Kimura, Y. Sugahara, K. Kuroda, *Phosph. Res. Bull.* 6 (1996) 205.
- [5] T. Kimura, Y. Sugahara, K. Kuroda, *J. Chem. Soc., Chem. Commun.* (1998) 559.
- [6] T. Kimura, Y. Sugahara, K. Kuroda, *Chem. Mater.* 11 (1999) 508.
- [7] Feng, Y. Xia, J. Feng, X. Bu, G.D. Stucky, *J. Chem. Soc. Chem. Commun.* (1997) 949.
- [8] S. Ayyappan, C.N.R. Rao, *J. Chem. Soc. Chem. Commun.* (1997) 575.
- [9] B. Chakraborty, A.C. Pulikottil, S. Das, B. Viswanathan, *J. Chem. Soc. Chem. Commun.* (1997) 911.
- [10] D. Zhao, Z. Luan, L. Keven, *J. Chem. Soc. Chem. Commun.* (1997) 1009.
- [11] M.P. Kapoor, Anuj Raj, *Appl. Catal. A* 203 (2000) 311.
- [12] X.S. Zhao, G.Q. (Max) Lu, *Micro. Meso. Mater.* 44-45 (2001) 185.
- [13] Ch. Subrahmanyam, B. Viswanathan, T.K. Varadarajan, *Eurasian Chem Tech Journal* (in press).
- [14] Ch. Subrahmanyam, B. Louis, F. Rainone, B. Viswanathan, A. Renken, T.K. Varadarajan, *Catal. Commun.*, 3 (2002) 45.
- [15] D. Zhao, Z. Luan, L. Kevan, *J. Phys. Chem.*, 101 (1997) 6943.
- [16] Ch. Subrahmanyam, B. Louis, F. Rainone, B. Viswanathan, A. Renken, T.K. Varadarajan, *Appl. Catal: A Gen.*, 3 (2002) 45.
- [17] S.K. Mahapatra, B. Sahoo, W. Kenue, P. Selvem, *Chem. Commun.* (2002) 1466.
- [18] J. C. Vartuli, K.D. Schmitt, C. T. Kresge, W.J. Roth, M. E. Leonowicz, S. B. McCullen, S. D. Hellring, J. S. Beck, J.L. Schlenker, D. H. Olson, E. W. Sheppard, *Chem. Mater.* 6 (1994) 2317.
- [19] T. Sen, P. R. Rajamohanam, S. Ganapathy, S. Sivasankar, *J. Catal.*, 163 (1996) 354.
- [20] M. Chatterjee, T. Iwasaki, H. Hayashi, Y. Onodera, T. Ebina, T. Nagase, *Chem. Mater.* 11 (1999) 1368.
- [21] Tapas Sen, Maya Chatterjee, S. Sivasanker, *J. Chem. Soc. Chem. Commun.* (1995) 207.
- [22] P.H. Hari Prasad Rao, A. A. Belhekar, S.G. Hegde, A. V. Ramaswamy, P. Ratnasamy, *J. Catal.*, 141 (1993) 595.