



Probing Cobalt Sites in CoAPO-11 via Spectroscopic and Activity Studies

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Received: 31 March 2017;

Accepted: 30 May 2017;

Published online: 31 August 2017;

AJC-18518

A systematic study undertaken for the oxidation state, coordination, stability of cobalt in CoAPO-11 structure by means of spectroscopic and catalytic activity, is presented. AlPO-11 containing Co(II) in the tetrahedral coordination was indicated by powder diffraction, electronic and EPR data. During calcination of Co(II) was partly converted to Co(III) and reverted back to Co(II) upon exposure to atmosphere. Apart from micropores, CoAPO-11 sample contains mesopores, which possibly arise from interparticle void space. The tetrahedral location of Co(II) was inferred from EPR data. The rectangular to spherical shapes of CoAPO-11 material was evident from electron micrographs. Activity studies revealed that *o*-cresol can selectively be converted to *o*-hydroxy benzoic acid. Moderate activity of CoAPO-11 along with spectroscopic analysis supports the fact that Co(II) is predominantly located in tetrahedral framework and do not convert to Co(III) effectively, as a consequence Co(II) are stable and do not display appreciable oxidative ability under mild reaction conditions.

Keywords: Aluminophosphate, CoAPO-11, *o*-Cresol.

INTRODUCTION

Aluminophosphate structures having corner sharing building units of AlO_4 and PO_4 tetrahedron possessing crystalline structure and well defined porous channel was first reported by Wilson and Flanigen [1] at Union Carbide have been subsequently gained significant attention in the field of catalysis, oil refining, petrochemicals and production of fine chemicals [2-4]. Compared to microporous zeolitic analogues, AlPO molecular sieves possess a larger variety of acid sites and broader acid sites distribution. Among the aluminophosphates, AlPO-11 having one dimensional pore system with a pore size of 6.3 Å belongs to the AEL topology, contains 10 ring hexagonal framework structure. Unlike the framework of a zeolite, AlPO-11 is neutral and thereby do not display appreciable catalytic functionality. However, a range of metals such as Fe, Ni, V, Ti, Cu, Zn, Mg, Mn, Cr, Mo *etc.* partly substitutes the framework aluminium in an AlPO which convert the substituted AlPO into an active oxidation and/or acid catalyst. Therefore, over the period several attempts have been made for isomorphous substitution of P(V) and/or Al(III) by transition metal ions to add catalytic functionalities [5-7]. Aluminophosphates (AlPO) have unique properties that can be used as hydrophilic adsorbents and their structure makes them excellent catalysis themselves for isomerization and oxidation of light paraffins [8]. Because of these valuable application

metals aluminophosphate (MeAPO) emerged as one of the important catalytic materials for reaction in heterogenous catalysis.

Among the metaloaluminophosphates (MeAPO), CoAPO-11 represents one of the most proficient oxidation catalytic systems. Several Co-substituted AlPOs have been synthesized and characterized by employing a range of spectroscopic techniques [9]. Among the divalent metals studied, cobalt containing AlPOs have attracted considerable attention due to variable oxidation state of cobalt renders the solid a redox catalyst [10]. Active cobalt sites can be inserted into the microporous AlPO-11 during synthesis, which facilitates the successful incorporation of a hydrolyzable metal cation and restricts the precipitation of their hydroxides along with improving stability. Thomas and Raja have established the substitution of metal ions particularly in AlPOs give rise to obtain heterogeneous catalysts [11]. Further, the recent works on aluminophosphate based mesoporous as well as micro-mesoporous hybrid materials have broadened the scope of future application of these materials [12-14]. It is largely believed that isomorphous substitution of a Al(III) by Co(III) results in a overall neutral and oxidation catalyst. On the other hand, replacement of Al(III) by Co(II) leads to a Bronsted acid sites [15]. The oxidative ability of CoAPO-11 materials have been attributed to the interconversion of Co(II) and Co(III) during the reaction.

Many researchers [16,17] have carried out the synthesis of cobalt containing AlPO-11 by adopting different methods and evaluated the catalytic properties in various organic transformations [17]. Apart from usual techniques such as XRD, TG and FT-IR [18,19], a variety of spectroscopic methods including DRUV-VIS [19] and EPR [20] were employed to probe the location and oxidation state of cobalt in the aluminophosphate matrix. Beyond the spectroscopic investigation, reactivity assessment is an important method to probe the cobalt sites. Cobalt has the ability of activating molecular oxygen, therefore can be used as a potential oxidation catalyst and some important contributions are discussed below. Cobalt(II) substituted CoAPO-11 catalyst was studied with cyclodehydration of butanol for the production of tetrahydrofuran in which acidic behaviour was attributed for the catalytic performance [21]. Yumin *et al.* [22] investigated oxidation reaction of *p*-cresol in presence of sodium hydroxide to protect the -OH group and alkyl group undergoes oxidation reaction. They have proposed a mechanism in which Co(III) plays a vital role in initiating and propagating the reaction. At the same time, results showed that Co(III) has better activity and selectivity than Co(II). It has been reported that *p*-cresol can be oxidized to *p*-hydroxy benzyl alcohol and eventually oxidized to *p*-hydroxy benzaldehyde [16]. Among many synthetic methods, liquid phase catalytic oxidation of *p*-cresol with molecular oxygen appears most promising [23]. Varying cobalt in Co-saponite showed the highest conversion of 92 % with > 90 % selectivity to *p*-hydroxy benzaldehyde for liquid phase oxidation of *p*-cresol under mild conditions [23]. Tian *et al.* [18] reported that oxidation of cyclohexane over a series of metal containing AlPOs in presence of molecular oxygen as oxidant and observed that CoAPO-11 was the best catalyst yielding cyclohexanol selectively. Oxidation of *ortho/para*-cresol was studied by She *et al.* [24] to obtain corresponding hydroxy benzaldehyde by using cobalt porphyrin complexes under homogeneous condition using NaOH and described that the electronic factor associated with the ligand plays a decisive role in controlling the selectivity of the product. Compounds like hydrotalcite have been used as catalyst to get a high *p*-cresol conversion. The autoxidation of *p*-cresol to *p*-hydroxy benzaldehyde by using CoCl₂, CoAPO-5 and CoAPO-11 catalysts in methanolic sodium hydroxide solution were conducted [16] and observed activity is solely attributed to the cobalt species present in homogenous medium, *i.e.* cobalt is unstable in AlPO framework and released into reaction medium during reaction.

Although considerable progress has been made to unravel the oxidation state, coordination and location of cobalt in aluminophosphate structure, still ambiguity remains regarding role of cobalt species in catalysis. The present study relates to the hydrothermal synthesis and systematic characterization of cobalt containing aluminophosphate-11 (CoAPO-11) structure. CoAPO-11 samples were characterized by various analytical and spectroscopic techniques. Catalytic performance of the CoAPO-11 was evaluated by performing liquid phase oxidation of *o*-cresol. The probable structure property correlation has been reported. While most of the earlier investigations focused on spectroscopic studies, we have attempted to relate both the spectroscopic data and catalytic activity performance

in order to understand the oxidation state, location and role and stability of cobalt in catalysis.

EXPERIMENTAL

Synthesis of CoAPO-11: Microporous CoAPO-11 was synthesized by hydrothermal method following the procedure reported by Wilson and Flanigen [1] with the following gel composition; 1.0 Al₂O₃: 1.0 P₂O₅: 1.0 DPA: 0.1 CoO: 40 H₂O. Aluminium isopropoxide was used as the source of aluminium, dipropylamine as structure directing agent and orthophosphoric acid as a source of phosphorus. Aluminium isopropoxide was kept in ageing overnight for the complete dissolution of the mixture. An appropriate amount of orthophosphoric acid was added with water and the resulting mixture was stirred for 2 h. Then desired amount of cobalt nitrate was added and the resulting mixture was allowed to stir for another 2 h. Dipropylamine was added and the mixture was stirred for another 2 h. The gel was transferred to a 175 mL autoclave lined with Teflon and kept under aging at 448 K for 24 h. The product was filtered, washed repeatedly with distilled water and dried at 363 K overnight. The synthesized sample was calcined in order to remove the template by increasing the temperature from room temperature to 823 K at a rate of 1 K min⁻¹ under flow oxygen. The sample was kept at 823 K for 6 h and then cooled to room temperature under the flow of oxygen.

Characterization: Both as-synthesized and calcined CoAPO-11 were characterized systematically by various spectroscopic and analytical techniques. Powder X-ray diffraction (XRD) patterns were recorded using Brucker D8 diffractometer with Cu K_α radiation. The diffraction patterns were recorded in the 2θ range of 5-50°, with a scan speed and step size of 0.5° min⁻¹ and 0.02°, respectively. Thermogravimetric analysis (TGA) was performed under air with a Toledo-Mettler TG/DTA/851 system. Fourier transform infrared (FT-IR) spectra were recorded at room temperature on a Perkin Elmer 2000-FT IR in the range 4000-400 cm⁻¹ using KBr as a medium. Diffuse reflectance ultraviolet and visible (DRUV-Vis) spectra were recorded in the range 200-800 nm on Agilent Cary 100 UV-visible spectrophotometer using barium sulphate as the reference. BET-surface area and pore size were determined by analyzing the nitrogen adsorption-desorption isotherm at 77 K, using ASAP 2020, Micromeritics analytical system. The crystal morphology of the materials was determined with scanning electron microscopy (FESEM) by using Zeiss supra 40 vp instrument. Further, the morphology of the materials was investigated with the aid of transmission electron microscopy (TEM; Philips, CM200) operated at 20-200 kV. Electron paramagnetic resonance (EPR) pattern was recorded in a Varian machine at room temperature using tetracyanoethylene as standard in the field range from 80-600 gauss.

Catalytic reaction: In a typical catalytic reaction, *o*-cresol (1 mmol, 0.108 g), acetonitrile (4 mL), catalyst (100 mg) and 35 % aqueous H₂O₂ or *tert*-butyl hydroperoxide (TBHP, 2 mmol) were placed in a double neck round bottomed flask attached with condenser and allowed to react for 2-12 h in the temperature range 343-353 K. The products were analyzed using gas chromatography (Agilent 7890) connected to a HP-5 capillary column and flame ionization detector (FID). Substrate

conversion and product selectivity were determined using calibration plots and standard reference samples.

In order to verify the stability of cobalt during reactions, leaching tests were conducted as per the procedure described below. Approximately 100 mg of sample was treated with 5 mL of acetonitrile and 2 mL of *tert*-butyl hydroperoxide and stirred for 333 K for 12 h. The sample was filtered, the filtrate was collected and electronic spectra were recorded. Similarly, electronic spectra were recorded for acetonitrile and *tert*-butyl hydroperoxide containing cobalt nitrate and without cobalt nitrate for comparison purpose.

RESULTS AND DISCUSSION

Catalyst colour: The colour of the as-synthesized CoAPO-11 was royal blue in colour, which often considered the presence of Co(II) in the tetrahedral aluminophosphate framework [20]. After calcination the colour of the sample was changed to blue green which is usually assigned to presence of Co(III) ions. However, gradually the colour of calcined sample reverted back to blue maintaining Co(II) in tetrahedral coordination [25].

Powder X-ray diffraction: XRD patterns of the as-synthesized and calcined CoAPO-11 are shown in Fig. 1 and the patterns corresponded well to the AEL structure [1]. Formation of CoAPO-11 structure is indicated by appearance of several strong and weak reflections. Strong reflections at $2\theta = 9.5, 20.4, 21.1, 22.1, 22.7$ and 23.2 attributed to the planes (020), (310), (002), (231), (112) and (240) respectively. Several weak reflections at $2\theta = 8.1, 13.2, 15.7, 24.6, 26.6, 28.6, 31.6, 32.9, 34.2, 37.8$ assigned to the planes (110), (200), (121), (150), (132), (042), (161), (152), (123), (233) were also observed. CoAPO-11 is similar to the reflection pattern, which refers that AEL structure is retained with cobalt insertion. Further incorporation of the cobalt into the AlPO-11 structure did not alter the ordered AEL structure. Also calcination of CoAPO-11 did not result any collapse of the structure, which is supported by absence of any signature of cobalt impurity phase in the X-ray analysis.

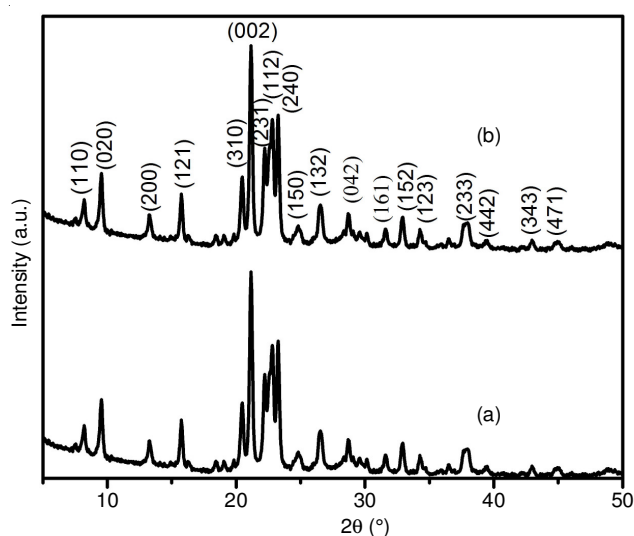


Fig. 1. XRD pattern of CoAPO-11: (a) as-synthesized (b) calcined

Thermogravimetric: Fig. 2 shows thermogravimetric pattern of as-synthesized CoAPO-11. About 10 % of total weight loss is observed in the thermogravimetry pattern of

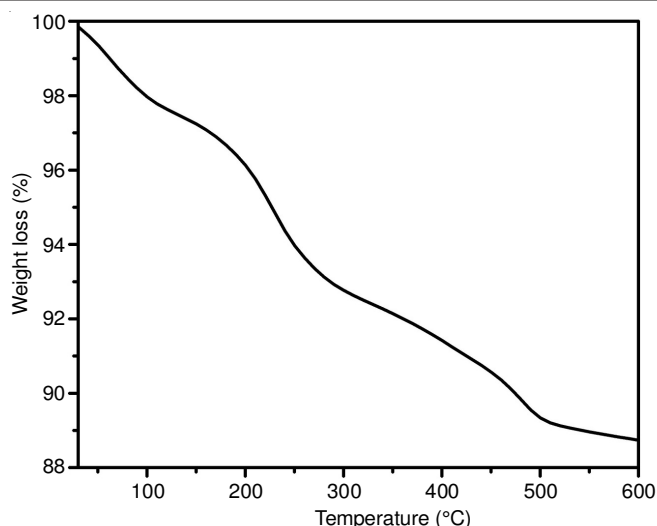


Fig. 2. TG plot of as-synthesized CoAPO-11

CoAPO-11 in which 1.5 % of weight loss occurred in the initial step corresponded to desorption of physically adsorbed water molecule, 4.7 % weight loss occurred in the second step corresponded to desorption of template desorption and in the third step 3.9 % weight loss ascribed to the combustion of organic species occluded in the channels of CoAPO-11 which refers to the porous nature of material [18].

BET-surface area: The N_2 adsorption-desorption isotherm of CoAPO-11 molecular sieve is shown in Fig. 3. The adsorption isotherm in pressure range $p/p_0 = 0.3$ confirms the typical microporous nature of CoAPO-11. A broad and flat hysteresis observed between $p/p_0 = 0.4$ to 1.0 is possibly due to meso/macro porosity arising out of interparticle void space. Typical BET surface area measurement resulted in a value of $128 \text{ m}^2 \text{ g}^{-1}$ for CoAPO-11, which is an indicative of the microporous nature of CoAPO-11 [26]. Pore volume was estimated to be about $0.1 \text{ cm}^3 \text{ g}^{-1}$. The pore size determined both by BJH and DFT showed between $90\text{--}380 \text{ \AA}$, which falls in the mesopore region.

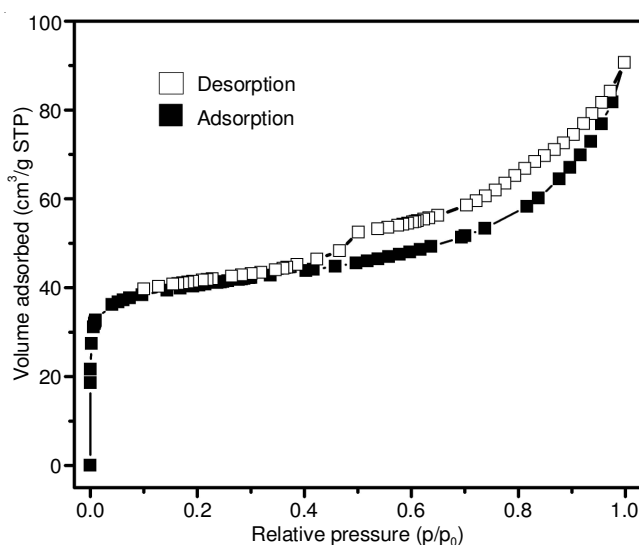


Fig. 3. N_2 adsorption-desorption isotherm of calcined CoAPO-11

FT-IR: Fig. 4 shows the FT-IR pattern of as-synthesized and calcined CoAPO-11. Bands appearing at 3606 and 3445

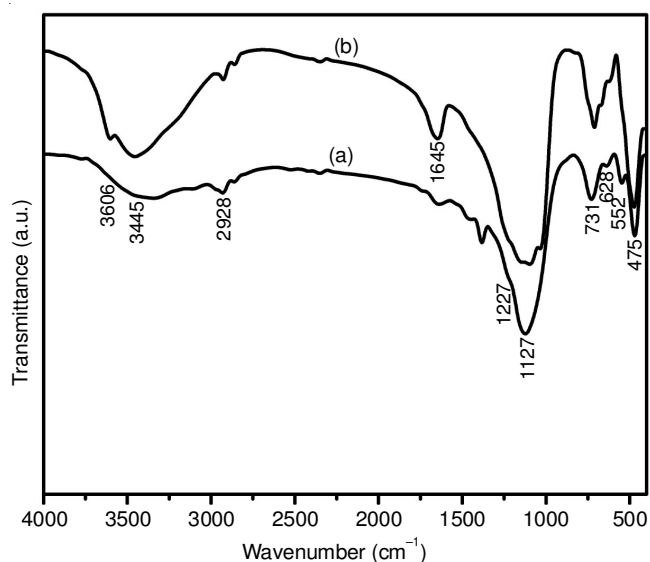


Fig. 4. FT-IR spectra of CoAPO-11: (a) as-synthesized (b) calcined

cm^{-1} vibration can be assigned to $\nu(\text{P-OH})$ and $\nu(\text{CoP-OH})$ bridged OH groups interacting with the oxygen atoms of the framework [27]. Band at 1645 cm^{-1} ascribed to the bending mode of $-\text{OH}$ group. Similarly bands at 1227 and 1031 cm^{-1} are attributed to the asymmetrical stretching vibration of exterior Al-O-P and Al-O-Co. The shoulder band appeared at 1227 cm^{-1} is considered as an evidence that Co(II) is incorporated into the framework of AlPO-11 [27]. Bands observed at 1127 and 731 cm^{-1} are assigned to interior asymmetrical and symmetrical stretching vibration of AlO_4^- and PO_4^+ tetrahedral [27]. Two weak bands at 628 and 552 cm^{-1} assigned to the distortion vibration of four membered rings and six-membered rings structure of AlPO-11 is also observed. The band at 475 cm^{-1} is attributed to the bending vibration of the AlPO-11 double ring.

DR UV-visible spectra: Fig. 5 shows UV-visible spectra of both as-synthesized and calcined CoAPO-11. Three absorption peaks observed both in as-synthesized and calcined at 535 , 580 and 630 nm indicate the presence of cobalt in the tetrahedral environment *i.e.* incorporated into the framework of AlPO-11 [19]. The triplet bands are assigned to the $^4\text{A}_2(\text{F}) \rightarrow ^4\text{T}_1(\text{F})$, $^4\text{A}_2(\text{F}) \rightarrow ^4\text{T}_1(\text{P})$ and $^4\text{A}_2(\text{F}) \rightarrow ^4\text{T}_2(\text{F})$ *d-d* transition of the divalent cobalt ions in tetrahedral coordination. From the studies of UV-visible spectra Sponer *et al.* [19] have concluded that cobalt was present as Co(II) in cobalt containing aluminophosphate molecular sieves and did not change its valence during calcination. Upon calcination, the colour of CoAPO-11 was turned to blue green, however the electronic absorption pattern remained the same. Such a trend is attributed to distortion in tetrahedral Co(II) coordination. Appearance of band in the region $250\text{--}500 \text{ nm}$ is often considered as a signature of Co(III) [28], nevertheless in the present study such bands are not noticed clearly, hence the presence of Co(III) was excluded.

Electron paramagnetic resonance spectra: The EPR patterns of as-synthesized and calcined CoAPO-11 recorded at room temperature are shown in Fig. 6. Both as-synthesized and calcined CoAPO-11 showed signals g_{eff} at 1.9 and 3.7 assigned to Co(II) in a tetrahedral environment and in a compressed tetrahedral environment, respectively. The broad

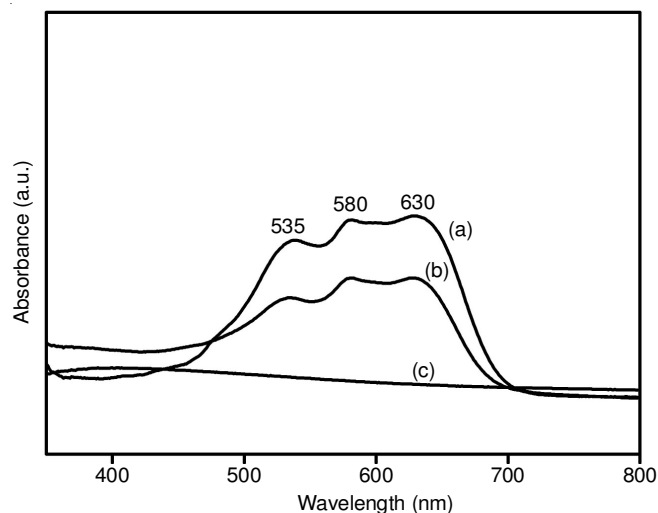


Fig. 5. DRUV-Vis absorption spectra of CoAPO-11: (a) as-synthesized (b) calcined and (c) calcined APO-11

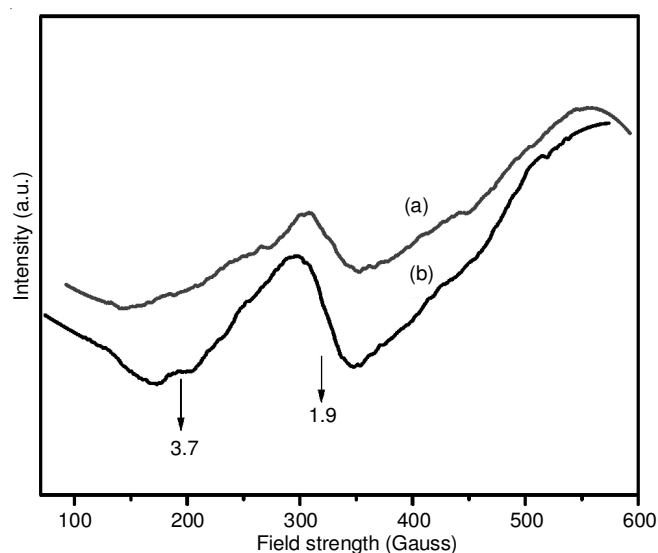


Fig. 6. EPR of CoAPO-11: (a) as-synthesized (b) calcined

feature signal centered g_{eff} at 3.7 is due to high spin electronic configuration [20]. Further both as-synthesized and calcined CoAPO-11 showed signals having same line width of 47 gauss. The relative intensity, *i.e.*, intensities of g_{eff} 1.9 to 3.9 was estimated and found to be equal, which indicates the concentration of cobalt species remains same both in as-synthesized and calcined sample.

Field emission scanning electron microscope: The particle size and morphology of CoAPO-11 was probed by FESEM and the micrographs are presented in Fig. 7. The FESEM revealed uniform sized, spherical to distorted spherical shapes having dimension between $10\text{--}15 \mu$ [27]. At higher resolution non-uniform and surface roughness appeared showing rectangular shape rods having average size of about 5μ . Fig. 8 shows the EDAX in which the sample contains Al, P, Co and O. The elemental composition (in wt %) of CoAPO-11 determined by EDAX analysis was Co (0.68), Al (19.36), P (19.39), O (60.58). The cobalt content in the precursor gel was $0.8 \text{ wt } \%$, which is approximately 15% less in the final CoAPO-11. The shapes of crystals appeared to cuboid to

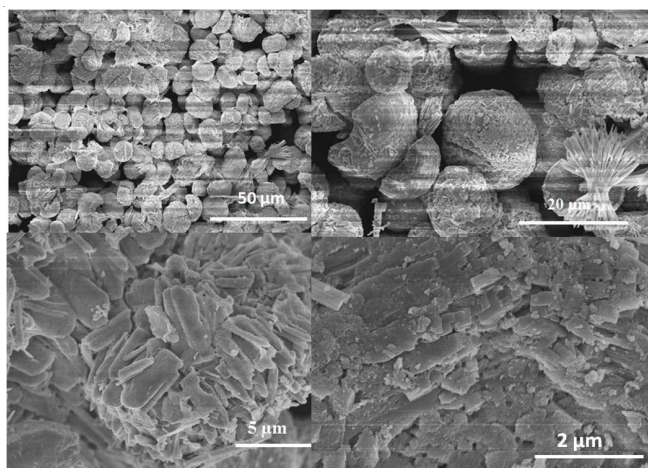


Fig. 7. FESEM of calcined CoAPO-11

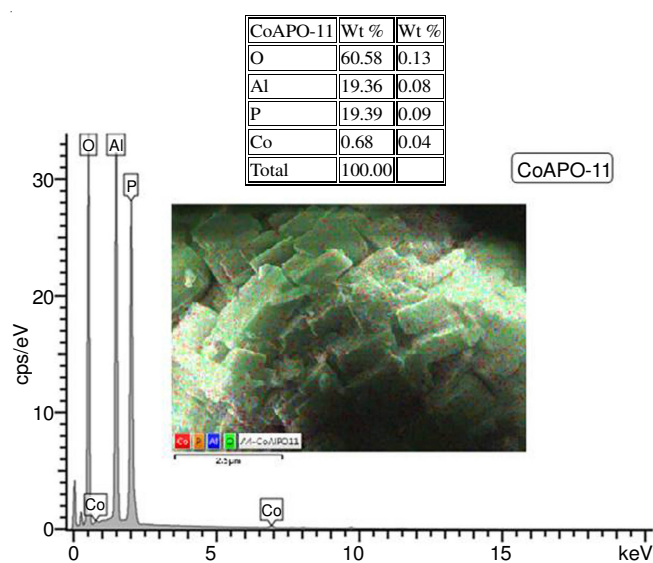


Fig. 8. EDAX of calcined CoAPO-11

spherical at higher resolution. As the magnification is increased the surface appears to have made up of rectangular crystallites having average dimension of about $2\ \mu$ seen in Fig. 7(c). Further magnification showed the plenty of irregular surface roughness/macroscopic voids [Fig. 7(d)].

Transmission electron microscope: TEM patterns are shown in Fig. 9 reveals the needle shaped and uniform morphology of CoAPO-11 [29]. The electron diffraction pattern clearly showed the crystalline nature of the CoAPO-11 material. The crystal sizes were in the range of 4–10 nm. The bright spots in

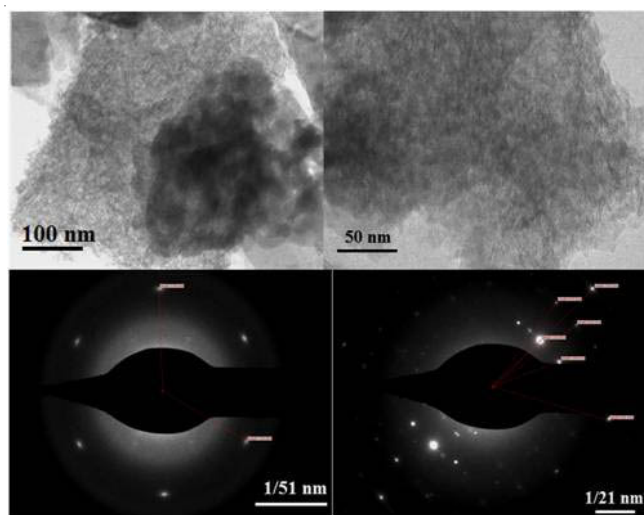


Fig. 9. TEM of calcined CoAPO-11

the electron diffraction patterns show different crystal planes present according to probability. The observed electron diffraction pattern at 2.7 and 2.5 Å is attributed to the reflections (123) and (233) respectively. The d-values determined by electron diffraction patterns are in well agreement with the powder XRD pattern. Further, aggregation of oxidic phases of cobalt was not observed in electron micrographs.

Reactivity studies: The catalytic performance of CoAPO-11 was evaluated by performing oxidation of *o*-cresol in liquid phase using TBHP and H_2O_2 as the oxidant and results are summarized in Table-1. *o*-Hydroxy benzaldehyde, *o*-hydroxy benzoic acid and *o*-hydroxy benzyl alcohol were obtained as oxidized product (**Scheme-I**). During the reactivity studies we have achieved a maximum of 9.3 % substrate conversion and *o*-hydroxy benzoic acid being the predominant product, irrespective of variation in reaction conditions. For example increase in temperature did not result remarkable increase in substrate conversion. With the variation of the oxidant, H_2O_2 to TBHP the substrate conversion was decreased. Extending the reaction studies in presence of TBHP in water or TBHP in decane did not yield any noticeable enhancement in catalytic performance (entry 4–7). The oxidative ability of cobalt in an aluminophosphate matrix is largely attributed to the interplay between Co(II) and Co(III) state [29] and lack of Co(III) sites as evident from spectral studies, possibly results in moderate performance of CoAPO-11.

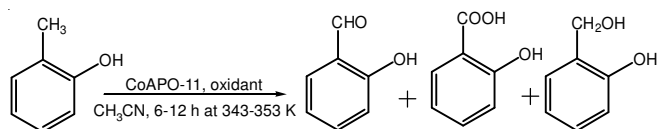
The possibility of dissolution of CoAPO-11 framework and leaching of cobalt into homogeneous medium to catalyze

TABLE-1
CATALYTIC OXIDATION OF *o*-CRESOL OVER CoAPO-11

Entry	Temperature (K)	Oxidant	Duration (h)	Substrate conversion (%)	Selectivity (%)		
					S-CHO	S-COOH	S-CH ₂ OH
1	343	H ₂ O ₂	7	9.3	11.5	59.7	28.6
2	353	H ₂ O ₂	7	7.2	8.9	58.7	33.0
3 ^a	343	H ₂ O ₂	7	1.7	—	100	—
4 ^b	343	TBHP	12	—	—	—	—
5 ^c	333	TBHP	7	—	—	—	—
6 ^d	333	TBHP	10	—	—	—	—
7 ^e	333	TBHP	10	—	—	—	—

Reaction conditions: *o*-cresol (1.0 mmol); Oxidant (2.0 mmol); catalyst: 10 mg; solvent (acetonitrile): 4 mL

^aH₂O₂ without CoAPO-11; ^bTBHP in water; ^cTBHP in water and CoAPO-11; ^dTBHP in decane; ^eTBHP in decane and CoAPO-11



Scheme-I: Reaction profile of *o*-cresol over CoAPO-11

the reaction was verified *via* leaching tests. The electronic spectra recorded for different solutions are shown in Fig. 10. As it can be seen clearly, filtrate obtained from treatment of CoAPO-11 and acetonitrile/TBHP alone produced similarly pattern. The presence of cobalt in the filtrate cannot be unambiguously established. Further, we recorded the spectrum of cobalt salt mixed with acetonitrile/solvent system and the result showed a distinct broad band between 400-600 nm having $\lambda_{\max}$ at 508 nm [30] assigned to Co(II) in tetrahedral and/or octahedral coordination. Therefore, non-appearance of any signal of cobalt in the filtrate excludes the possibility of dissolution of CoAPO-11 matrix under reaction conditions. These studies strongly validate the fact that under present set up, divalent cobalt is stable in the CoAPO-11 structure and unlikely to catalyze the oxidation reaction under mild reaction conditions.

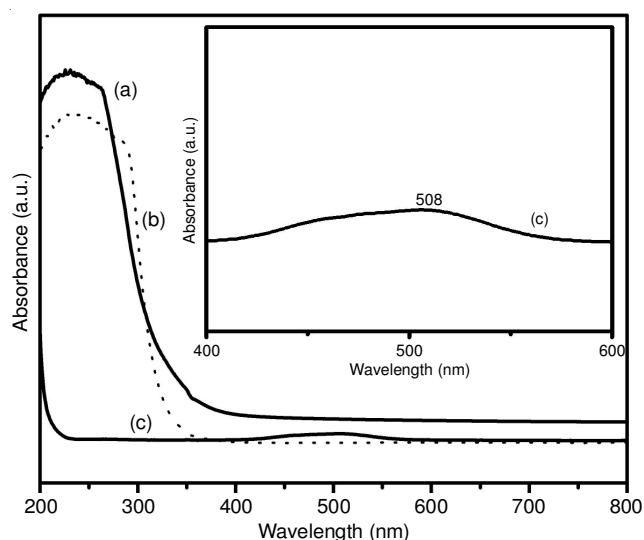


Fig. 10. DRUV-visible absorption spectra of: (a) Filtrate of washed catalyst (b) Oxidant in acetonitrile (c) Co(II) salt in homogeneous medium

Conclusion

In the present study, the successful synthesis of crystalline and pure microporous CoAPO-11 was achieved. As evident from various spectroscopic investigation cobalt predominantly remained as Co(II) in the tetrahedral framework of AlPO-11. CoAPO-11 samples were observed to have uniform shape, nevertheless possessed considerable amount of surface roughness/void space. The absence of Co(III) in CoAPO-11 do not favour an interconversion between Co(II) and Co(III). As a consequence catalytic performance of CoAPO-11 was moderate towards oxidation of *o*-cresol under the chosen mild reaction conditions. Further Co(II) was found to be stable in the matrix and it remained intact during the reactions, without leaching into the solutions.

ACKNOWLEDGEMENTS

One of the authors, SS thanks University Grants Commission, New Delhi, India for the award of Basic Scientific Research fellowship. The authors are indebted to Prof. A. Sakthivel,

Department of Chemistry, Delhi University, Delhi, India for extending laboratory facility to carry out certain measurements.

REFERENCES

- S.T. Wilson and E.M. Flanigen, Crystalline Metal Aluminophosphates, US Patent 4567029 (1986).
- L.E. Iton, I. Choi, J.A. Desjardins and V.A. Maroni, *Zeolites*, **9**, 535 (1989); [https://doi.org/10.1016/0144-2449\(89\)90051-1](https://doi.org/10.1016/0144-2449(89)90051-1).
- S. Dzwigaj, M. Briend, A. Shikholeslami, M.J. Peltre and D. Barthomeuf, *Zeolites*, **10**, 157 (1990); [https://doi.org/10.1016/0144-2449\(90\)90039-T](https://doi.org/10.1016/0144-2449(90)90039-T).
- B. Kraushaar-Czarnetzki, W.G.M. Hoogervorst, R.R. Andréa, C.A. Emeis and W.H.J. Stork, *J. Chem. Soc., Faraday Trans.*, **87**, 891 (1991); <https://doi.org/10.1039/FT9918700891>.
- N. Rajic, D. Stojakovic and V. Kaucic, *Zeolites*, **10**, 802 (1990); [https://doi.org/10.1016/0144-2449\(90\)90066-Z](https://doi.org/10.1016/0144-2449(90)90066-Z).
- J.M. Bennett and R.M. Kirchner, *Zeolites*, **12**, 338 (1992); [https://doi.org/10.1016/0144-2449\(92\)90027-M](https://doi.org/10.1016/0144-2449(92)90027-M).
- N. Zabukovec, N. Golic, P. Fajdiga and V. Kaucic, *Zeolites*, **15**, 104 (1995); [https://doi.org/10.1016/0144-2449\(94\)00029-R](https://doi.org/10.1016/0144-2449(94)00029-R).
- H.O. Pastore, S. Coluccia and L. Marchese, *Ann. Rev. Mater. Res.*, **35**, 351 (2005); <https://doi.org/10.1146/annurev.matsci.35.103103.120732>.
- A. Verberckmoes, B.M. Weckhuysen and R.A. Schoonheydt, *Micropor. Mesopor. Mater.*, **22**, 165 (1998); [https://doi.org/10.1016/S1387-1811\(98\)00091-2](https://doi.org/10.1016/S1387-1811(98)00091-2).
- N. Venkaththri and G.P. Aswin Kumar, *Indian J. Chem. Technol.*, **11**, 843 (2004).
- J.M. Thomas and R. Raja, *Chem. Rec.*, **1**, 448 (2001); <https://doi.org/10.1002/tcr.10003>.
- A.K. Singh, R. Yadav and A. Sakthivel, *Adv. Por. Mater.*, **4**, 54 (2016); <https://doi.org/10.1166/apm.2016.1090>.
- R. Yadav and A. Sakthivel, *Appl. Catal. A*, **481**, 143 (2014); <https://doi.org/10.1016/j.apcata.2014.05.010>.
- R. Yadav, A.K. Singh and A. Sakthivel, *Catal. Lett.*, **146**, 800 (2016); <https://doi.org/10.1007/s10562-015-1688-z>.
- S.T. Wilson and E.M. Flanigen, *ACS Symp. Ser.*, **398**, 329 (1989); <https://doi.org/10.1021/bk-1989-0398.ch023>.
- M.P.J. Peeters, M. Busio and P. Leijten, *Appl. Catal. A*, **118**, 51 (1994); [https://doi.org/10.1016/0926-860X\(94\)80088-X](https://doi.org/10.1016/0926-860X(94)80088-X).
- P.E. Dai, R.H. Petty, C.W. Ingram and R. Szostak, *Appl. Catal. A*, **143**, 101 (1996); [https://doi.org/10.1016/0926-860X\(96\)00073-7](https://doi.org/10.1016/0926-860X(96)00073-7).
- P. Tian, Z. Liu, Z. Wu, L. Xu and Y. He, *Catal. Today*, **93-95**, 735 (2004); <https://doi.org/10.1016/j.cattod.2004.06.100>.
- J. Sponer, J. Cejka, J. Dedeczek and B. Wichterlova, *Micropor. Mesopor. Mater.*, **37**, 117 (2000); [https://doi.org/10.1016/S1387-1811\(99\)00258-9](https://doi.org/10.1016/S1387-1811(99)00258-9).
- V. Kurshev, L. Kevan, D.J. Parillo, C. Pereira, G.T. Kokotailo and R.J. Gorte, *J. Phys. Chem.*, **98**, 10160 (1994); <https://doi.org/10.1021/j100091a035>.
- S. Gurjar, U.S. Thakur and R. Tomar, *Int. J. Inst. Pharm. Life Sci.*, **4**, 5 (2015).
- L. Yumin, L. Shetian, Z. Kaizheng, Y. Xingkai and W. Yue, *Appl. Catal. A*, **169**, 127 (1998); [https://doi.org/10.1016/S0926-860X\(97\)00372-4](https://doi.org/10.1016/S0926-860X(97)00372-4).
- V.S. Kshirsagar, A.C. Garade, K.R. Patil, R.K. Jha and C.V. Rode, *Ind. Eng. Chem. Res.*, **48**, 9423 (2009); <https://doi.org/10.1021/ie801941e>.
- Y. She, W. Wang and G. Li, *Chin. J. Chem. Eng.*, **20**, 262 (2012); [https://doi.org/10.1016/S1004-9541\(12\)60387-5](https://doi.org/10.1016/S1004-9541(12)60387-5).
- S. Prasad and I. Balakrishnan, *Catal. Lett.*, **11**, 105 (1991); <https://doi.org/10.1007/BF00866907>.
- D. Li, J. Yao and H. Wang, *Prog. Nat. Sci. Mater. Int.*, **22**, 684 (2012); <https://doi.org/10.1016/j.pnsc.2012.11.003>.
- Z.H. Zhang, S. Hu, X.L. Han, B.J. Xu and Z.F. Yan, *J. Fuel Chem. Technol.*, **33**, 746 (2005).
- D.L. Wood and J.P. Remeika, *J. Chem. Phys.*, **46**, 3595 (1967); <https://doi.org/10.1063/1.1841263>.
- S. Sahoo and S.K. Badamali, *Adv. Porous Mater.*, **4**, 39 (2016); <https://doi.org/10.1166/apm.2016.1099>.
- F.A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, New York, end 3, p. 881 (1972).