

Understanding the role of acid sites of Zinc Aluminophosphate catalysts in eco-friendly synthesis of carbamates

Hamza Annath^{a,*}, Vijayasankar Viswambaram Aloor^{b,*} and Nagaraju Narasimhaiah^c

a) School of Chemistry and Chemical Engineering, Queen's University Belfast, Stranmillis Road, Belfast-BT9 5AG, United Kingdom

b) Department of Sciences & Humanities, Faculty of Engineering, CHRIST- Deemed to be University, Bengaluru- 560074, India

c) Catalysis Research Laboratory, St Joseph's college P.G. and Research Centre, Bengaluru 560027, India.

Received 2 January 2020; received in revised form 18 November 2020; accepted 26 January 2021

ABSTRACT

Aluminophosphate and metal incorporated aluminophosphates have been synthesized at ice-cold temperature by simple co-precipitation method in the absence of a templating agent. Surface and bulk properties of synthesized materials were studied by different characterization techniques. The materials were found to be X-ray amorphous. N₂ adsorption-desorption studies exhibited the existence of microporous structure and uniform narrow slit type of pores on the materials. The catalytic activity of the synthesized material was tested in phosgene free synthesis of carbamates from corresponding amines and dimethyl carbonate (DMC) through a greener route. Metal incorporated Aluminophosphates indicated excellent catalytic activity compared to pure aluminophosphates. Zinc aluminophosphate catalyst exhibited 83% carbamate yield with 100% selectivity towards the formation of carbamate. The excellent catalytic activity of Zinc aluminophosphate with 94% amine conversion is attributed to its surface properties mainly moderate acid strength. The incorporated metal plays a vital role in the structural and textural properties of aluminophosphates. A systematic study was conducted to correlate the catalytic activity and surface properties of metal aluminophosphates. Reaction conditions were optimized to obtain a better yield through phosgene free eco-friendly routes using different amines. The catalyst was found to be recyclable for 5 cycles in the desired reaction without a reduction in conversion and selectivity.

Keywords: Zinc aluminophosphates, Solid acid catalysts, Phosgene-free synthesis, Dimethyl carbonate, Organic carbamates.

1. Introduction

Organic carbamates are one of the most important intermediates in the fine chemical industry for the manufacture of isocyanates, agrochemicals, drugs and as amine protecting groups in organic synthesis [1-4]. Isocyanates are used as the monomers for the production of polyurethanes. The demand for polyurethanes in the automobile industry is increasing due to their light weight, strength and performance [5-6]. Conventionally the most applied method of isocyanates production is the thermal decomposition of carbamates. The carbamates, in turn, are produced from amines and phosgene or its derivatives, a highly toxic and corrosive raw material [7].

Another route followed for carbamate production is the reaction between toxic isocyanates and alcohols. Three well-known rearrangement reactions followed for the conversion of carboxylic acids to carbamates are the Curtius rearrangement of acyl azides [8], the Hoffmann rearrangement of carboxamides [9] and the Lossen rearrangement of hydroxamic acids [10]. All these methods are regarded as highly non-sustainable due to the toxicity of phosgene, corrosive nature of by-product hydrochloric acid and high energy investments. The most widely studied and explored non-phosgene alternative routes reported in the literature for carbamates synthesis are oxidative carbonylation of amines [11], reductive carbonylation of nitro compounds [12], alcoholysis of substituted urea [13] and alkoxy carbonylation of amines with dialkyl carbonates [7]. Corrosiveness of carbon monoxide, high

*Corresponding author:

E-mail address: h.annath@qub.ac.uk (H. Annath); avvijayasankar@gmail.com (V. V. Aloor)

cost and de-activation nature of noble metal-based catalysts, leads to non-eco-friendly routes for carbamate synthesis. Thus the development of environmentally friendly methods for the synthesis of carbamate is an important task in organic fine chemical synthesis. Dimethyl carbonate (DMC) is a versatile organic carbonate that can replace several toxic reagents such as methyl halides, dimethyl sulfides and phosgene in many industrially important organic transformations. The use of DMC as an alternative reagent in organic synthesis is greener because its building block is environmentally benign carbon dioxide and also its biodegradability [14].

In the last decade, many catalytic and non-catalytic approaches were reported for the synthesis of carbamates by methoxycarbonylation of amines. These reports include ceria, silver carbonate, potassium carbonate, deep Eutectic solvents, organostannanes as catalysts [15-19]. Alkoxides and alkyhalides are used as reactants along with amines and carbon dioxide for the production of carbamates [20, 21]. Complex separation protocols and expensive catalytic systems make these methods highly unfavourable. Environmentally benign routes using reusable, non-toxic heterogeneous catalysts such as Zinc salts, Al-SBA-15, Zinc incorporated berlinite materials and microcrystalline Zinc MOF were reported for the synthesis of carbamates [22-25]. Based on the earlier reports, a major disadvantage for the phosgene free synthesis of carbamates is mainly the availability of a low cost, non-toxic, recyclable catalyst prepared by a simple method.

Recently, we have reported using amorphous aluminophosphate and metal-incorporated aluminophosphates as catalysts for organic transformations [26-29]. These materials were prepared by simple precipitation methods in the absence of templating agents. Amorphous aluminophosphate and metal aluminophosphates materials contain weak acid-base as well as redox surface sites. The catalytic efficiency of these materials is highly influenced by the preparation conditions, such as pH of precipitation, type of precipitating agent, digestion of the precipitate, calcination temperature and type of transition metal incorporated to aluminophosphate. Thus there is a wide scope to develop metal incorporated aluminophosphates as a new class of heterogeneous catalysts for the synthesis of industrially important organic compounds.

In the present study, we have prepared metal phosphates (ZnP and AIP) and metal incorporated

aluminophosphates (ZnAIP and CuAIP) by co-precipitation methods in the absence of any surfactants or structure-directing molecules. Synthesised materials were characterized to understand their surface and bulk properties. The catalytic efficiency of ZnAIP and CuAIP has been investigated in methoxycarbonylation of an amine with DMC at ambient reaction conditions **Scheme 1**. A correlation between surface properties and catalytic activity has been made. The reaction conditions are optimized to obtain a better yield and a suitable mechanism is proposed.



Scheme 1. Reaction of Amine with dimethyl carbonate for the synthesis of carbamates

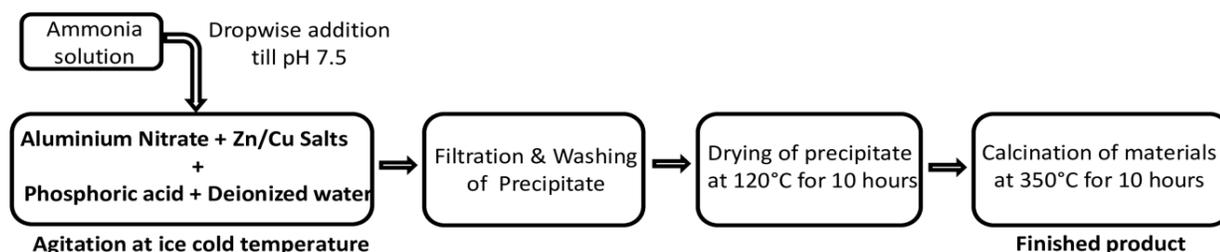
2. Experimental

2.1. Materials preparation

Pure and metal loaded

aluminophosphates were prepared by co precipitation method as per **Scheme 2** from the corresponding metal salts using 85% orthophosphoric acid as the phosphorous source and 28% ammonia solution as the precipitating agent [28]. Phosphorous to the total metal molar ratio (Al+M) was maintained as 1:1 in all preparations. Metal loaded aluminophosphate is abbreviated as MAIPn, where 'n' stands for the input mol percentage of metal and M represents either Cu or Zn. MAIPn was prepared by mixing aluminium nitrate [Al(NO₃)₃·9H₂O], metal nitrates of Cu or Zn and 85 % of H₃PO₄ in the desired molar ratio in 500 mL of de-ionized water at ice cold temperature to get a homogeneous solution. To the above clear solution, 28% liquor ammonia was added dropwise from a burette to obtain particles of high surface area, until a pH of 7.5 is reached. Aluminophosphate gel obtained was filtered, washed thoroughly with distilled water and dried at 120 °C in a hot air oven for 10 hours. The dried samples were powdered and further calcined at 350 °C for 5 hours.

Pure Aluminophosphates (AIP) was prepared by the same method followed for MAIPn in the absence of nitrates of Cu and Zn. Zinc aluminophosphate (ZnP) with 2.5 and 5 % of Zn was prepared by the same method followed for MAIPn in the absence of Aluminum nitrate.



Scheme 2. Preparation of metal aluminophosphates catalyst.(MAIP)

2.2. Material characterization

The elemental composition of materials was carried out in ICP-AES instrument (ARCOS from M/s. Spectro, Germany). 0.2 g of the sample was dissolved in concentrated HCL and diluted to 100 mL for analysis. The BET surface area and N₂ adsorption-desorption isotherms were determined using Micromeritics Tristar 3000 instrument. In a typical measurement, 0.2 g of the material screened through 40/60 mesh size was degassed at 250 °C for 2 hours in N₂ flow. After cooling to room temperature, adsorption-desorption analysis was conducted using N₂ as an adsorbate. The X-ray diffraction patterns of the materials were recorded using Rigaku instrument (Japan) with Cu K α radiation. FTIR spectra were recorded using Thermo-Scientific Nicolet IR-380 instrument by KBr pellet technique. Temperature-Programmed Desorption of Ammonia (TPD- NH₃) experiments was performed on a pulse Chemisorb instrument (Micromeritics). In a typical experiment, 0.15 g of material sieved through 40/60 mesh size was heated at 250 °C for 1 hour in He flow, cooled to room temperature and then 5 % NH₃ (balance nitrogen gas) was passed through the sample for 30 minutes. After purging with He atom for 10 minutes to remove excess ammonia present, the TPD-NH₃ was performed in the temperature range of 35–800 °C at a heating rate of 10 °C /min. The TCD signals were measured after 100 °C and a waiting time of 15 minutes to remove any physisorbed ammonia.

2.3. Catalytic activity test

The catalytic activity experiments were carried out in a two necked 100 mL round bottom (RB) flask with a reflux condenser fitted to one neck whereas the other neck was used for the sampling purpose. Calculated amounts of amine, DMC and the catalyst were taken in the RB flask and heated in an oil bath at a predetermined temperature. The reaction mixture was agitated using a magnetic stirrer, after a definite time the reaction mixture was cooled. Since DMC was used in excess quantity, no other solvents were added and the catalyst

was separated by filtration. The reaction mixture was analyzed using Thermo-Scientific GC (Chemito 8610) with 5% SE-30 packed column of length 8 ft. and diameter of 1.8 inch. The pure carbamate products were re-crystallized after evaporation of methanol by-product and DMC. The reaction products were also analyzed using GCMS.

2. Results and Discussion

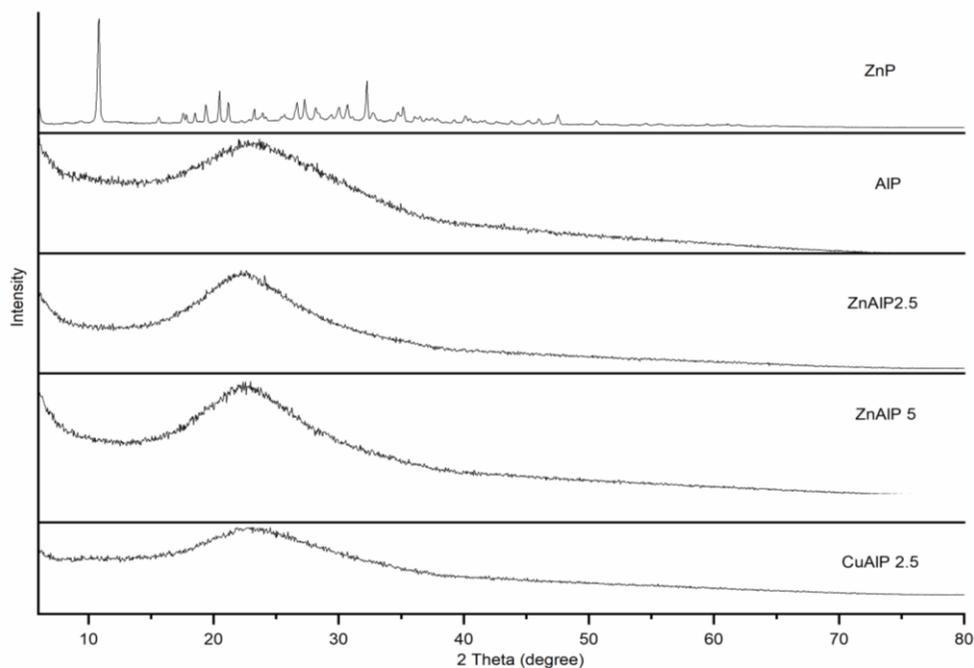
3.1. Surface and bulk properties

The data on the composition in terms of the atomic weight percentage of Zn/Cu, surface area, total pore volume, average pore diameter, surface acidity of all materials prepared for this study are given in **Table 1**. The atomic weight percentage of Zn/Cu is in close agreement with amounts incorporated during preparation this indicated complete precipitation of these metal ions. The surface area of AIP is significantly higher than ZnP. This is attributed to the formation of irregular microporous network structure in AIP due to the condensation of surface hydroxyl groups of adjacent aluminophosphate particles in the gel during high temperature calcination [30]. All bonds in aluminophosphates consist of a substantial amount of covalent character, in which both the phosphorus and the aluminium atom are tetrahedrally coordinated by oxygen. Alternative tetrahedral are joined through oxygen atoms to form continuous three-dimensional structures which geometrically resemble the known polymorphic forms of silica [31].

XRD analysis was carried out for determining the phases in the synthesized materials. All phosphate materials except ZnP were found to be amorphous with a broad XRD peak around 2 θ value of 25 (**Fig. 1**). The zinc phosphate demonstrated sharp peaks at 9.65, 31.29, 20 and 26.24 degrees. The crystalline hopeite structure of zinc phosphate materials was widely reported in the literature [32]. The hydrated Zn phosphate, Zn₃(PO₄)₃.4H₂O normally exists in orthorhombic system with cell dimensions a = 10.629 (2), b = 18.339 (3), c = 5.040 (1) Å.

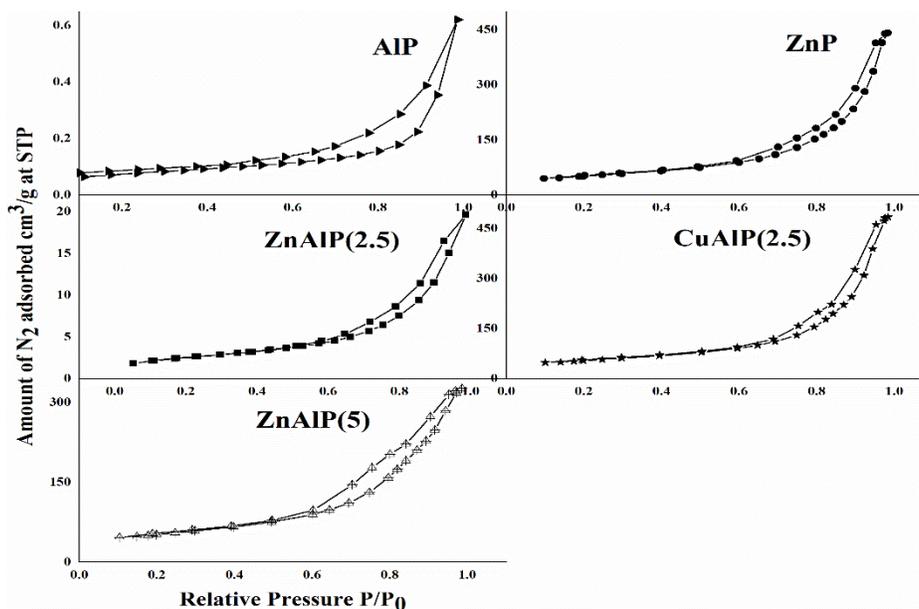
Table 1. Physico-chemical properties of metal phosphates and metal-aluminium phosphates

Material	Atomic weight % of Zn/Cu	BET surface area (m ² /g)	Average pore diameter (nm)	Pore volume (ml/g)	Total acidity (mmol/g)
AIP	-	181	10.9	0.5	0.1
ZnP	-	13	32.4	0.15	0.09
ZnAIP2.5	2.32	177	14.8	0.68	0.1
ZnAIP5	4.42	200	13.5	0.68	0.1
CuAIP2.5	1.93	188	15.5	0.74	0.12

**Fig. 1.** PXRD profiles of synthesized aluminophosphates and metal aluminophosphates

The N₂ adsorption-desorption isotherms of aluminophosphate and metal-aluminophosphates are given in Fig. 2. Significant changes were not observed

in the surface area of pure aluminophosphate by the incorporation of hetero elements Zn and/or Cu into aluminophosphates. However, there is a marginal increase in average pore diameter and total pore volume.

**Fig. 2.** N₂ adsorption-desorption isotherms of (a) ZnP, (b) AIP, (c) ZnAIP2.5, (d) ZnAIP5 and (e) CuAIP2.5

All samples showed type-V isotherm and H4 hysteresis loops with limiting adsorption. The H4 hysteresis attributes to capillary condensation within a narrow range of tubular pores, which confirms the high dimension of the pores [33]. The H4 type hysteresis isotherm also revealed the microporous structure of AIP and MAIPs with very narrow slit like pores.

The Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectra of synthesised materials are given in **Fig. 3**. Vibration band ($3600\text{--}3000\text{ cm}^{-1}$) centred at

3450 cm^{-1} due to OH stretching vibration band which is attributed to the surface hydroxyl groups, is associated with metal, aluminium and phosphorous atoms [34]. Absorption bands around 1640 cm^{-1} , are related to the presence of adsorbed carbon dioxide molecules. Peaks at $1100\text{--}1140\text{ cm}^{-1}$ are considered as characteristic absorption peaks are due to the asymmetric vibrations of phosphate. Shoulder peaks at 725 and 507 cm^{-1} due to the symmetric stretching mode of P-O-P and bending mode of O-P-O bonds respectively [35].

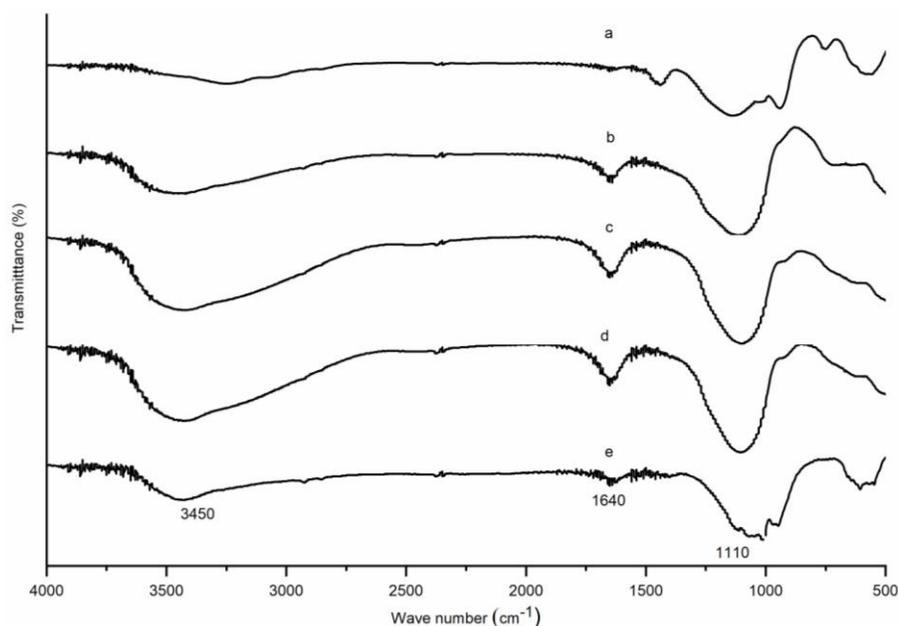


Fig. 3. FT-IR spectra of (a) ZnP, (b) AIP, (c) ZnAIP2.5, (d) ZnAIP5 and (e) CuAIP2.5

The acidic properties of all the materials are evaluated by NH_3 -TPD studies and this found that the acidity depended on the type of metal incorporated during the precipitation of aluminophosphate (**Fig. 4** and Table 1). ZnP contained strong acidic sites compared to pure aluminophosphate and metal aluminophosphates. The strong acidity of ZnP materials is attributed to the ionic character of the compound. Except for CuAIP2.5 the acid site strength of ZnAIP2.5 and ZnAIP5 materials are similar to AIP. The acid strength of CuAIP2.5 may be due to the formation of a greater number of Brönsted acidic sites. The anion vacancies formed by the substitution of trivalent Al or P by divalent metals may lead to the abstraction of the proton during the sol-gel transition which in turn might result in the Brönsted acid sites.

3.2. Catalyst performance

Performance of various catalyst systems used in the synthesis of carbamates by environmentally benign synthetic route using amine and dialkyl carbonate is given in **Table 2** [36-39]. It is observed that all reported

methods have limitations in terms of low yield or selectivity, high reaction temperature, long reaction time, complicated catalyst system, and complex product separation techniques etc. The catalytic performance of all the metal phosphates prepared in the present study was investigated in the methoxycarbonylation reaction (**Scheme 1**) between 1-butylamine and dimethyl carbonate (DMC). The percentage conversion of the amine, selectivity towards carbamate and yield of the carbamate are presented in **Fig. 5**. The conversion of amine ranged from 46 to 94% with 100% selectivity towards desired product and yield in the range of 31% to 83% was noticed.

A correlative study of catalytic activity based on conversion of n-butyl amine of the metal phosphates with their physico-chemical properties such as surface area, pore volume and total acidity exhibited the following trends.

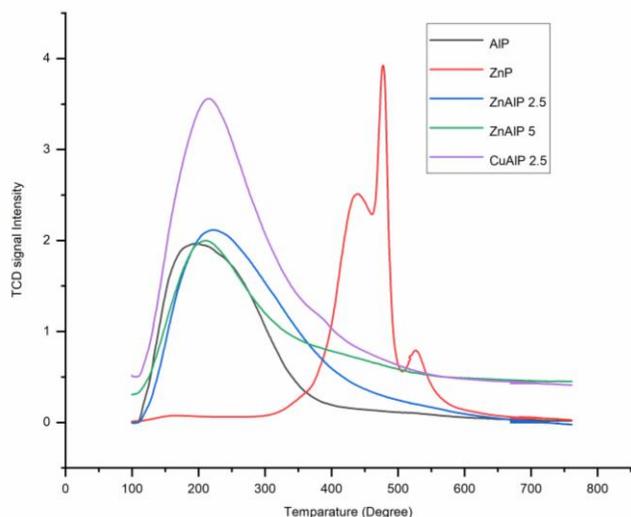


Fig. 4. NH₃-TPD profiles of aluminophosphates and metal aluminophosphates

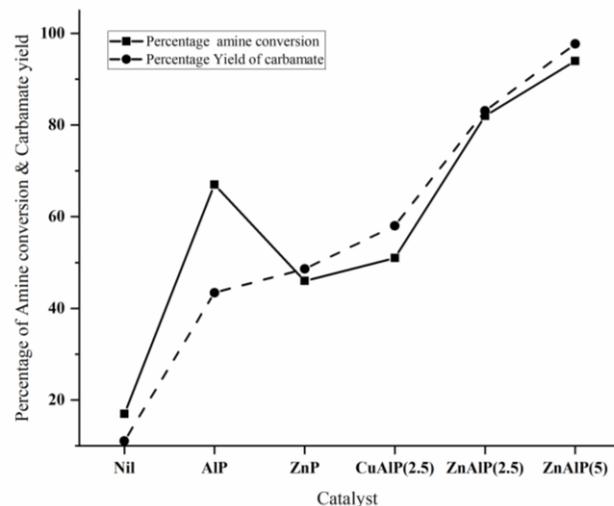


Fig. 5. Catalytic activity of aluminophosphates and metal aluminophosphates

Table 2. Catalytic activity of various catalysts reported for the synthesis of carbamates using amine and DMC

Catalyst	Conversion of amine (%)	Yield of carbamate obtained (%)	Reaction temperature (°C)	Reaction time (hour)	Reference
Al-SBA-15	93	84.2	70	35	23
Zr-MOF-808	98	93	120	20	25
Basic Zinc Carbonate	63	98	200	20	36
Sulfamic acid	-	59	100	8	37
Fr-Cr mixed oxide	67	52	150	24	38
Zn/Al/Pb mixed oxide	99	88	200	7	39

- %conversion: ZnP<CuAlP2.5<AIP<ZnAlP2.5 < ZnAlP5
- Total acidity: ZnP<ZnAlP5<AIP< ZnAlP2.5 < CuAlP2.5
- Surface area: ZnP<ZnAlP2.5<AIP<CuAlP2.5< ZnAlP5
- Total pore volume: ZnP<AIP<ZnAlP2.5<ZnAlP5< CuAlP2.5

3.3. Role of acidity on catalytic performance

The total acidity of the materials determined by ammonia TPD method is given in the **Table 1**. All materials contain almost similar acid strength varied from 0.09 to 0.12 mmol/g of ammonia but BET surface area varied significantly from 13 to 200 m²/g. Neither of these properties exhibited any direct correlation with the catalytic activity and the effect of the heterometal atom (Zn/Cu) was incorporated into AIP. However, a correlation was observed between the catalytic performance and acid strength distribution of metal phosphates (**Fig. 4**). ZnP exhibited the lowest catalytic activity even though it possesses strong acid sites based on TPD studies among the materials investigated. Further, all the other catalytic materials used for the present study indicated higher catalytic performance

than ZnP having surface acidic sites with lower strength. It is evident from the results obtained, that methoxycarbonylation between an amine and DMC is activated by acidic sites, but not necessarily by strong acid sites of catalysts.

The area and temperature of the TPD peak of CuAlP2.5 were attributed to a large number of acid sites with lower acid strength, but CuAlP2.5 exhibited low catalytic activity. This results further indicates that the number of acid sites on the catalytic material does not play a major role in the catalytic performance of the material. Hence it may be generalized from these studies, type of the acid site, such as Lewis or Brönsted type and their concentration to a great extent influence the catalytic performance of the metal phosphate materials.

Hydroxides, oxides and phosphates of Al, Cu and Zn are known to possess both Brönsted as well as Lewis acid sites on their surface. The metal species are the centers of Lewis sites whereas the surface hydroxyl groups contribute towards Brönsted acidity [40-41]. Zn²⁺ salts are known to be stronger Lewis acids than the Cu²⁺ salts. In the present study, ZnAlP2.5 showed higher catalytic

activity than CuAIP2.5. Percentage conversion of n-butylamine improved from 67 to 82 (Serial No. 3 of **Table 2**) when Zn^{2+} was incorporated into AIP. On the other hand the incorporation of Cu^{2+} reduced the conversion of AIP to 51%. Therefore, it may be inferred that the desired reaction is catalyzed to a greater extent by weaker Lewis acid sites of the metal aluminophosphate materials. Further, when the percentage of zinc increased from 2.5 to 5, in ZnAIP, the percentage conversion of the amine, and the yield of carbamate, also increased. Hence the relative amounts of Brönsted and Lewis acid sites on the catalysts seem to play a synergetic role in the synthesis of carbamate.

3.4. Optimization of reaction condition

These experiments were conducted to find the generality of the catalysts in methoxy carboxylation reaction. The main objective is to identify the optimum reaction conditions to obtain a better yield of carbamate through a greener route in presence of a reusable catalyst. For optimisation studies, among all the materials synthesised, we selected ZnAIP5 due to its better catalytic activity in the reaction between n-butylamine and DMC.

Catalytic conversion of different types of amines was tested and the results are presented in **Table 3**. All the primary amines converted into their respective carbamats but secondary amines failed to convert to carbamate. The steric hindrance occurred due to the Bulky tertiary butyl groups of secondary amines blocked the formation of carbamate. In the case of diamine, monomethoxy carbonylated product was formed, which results in lower selectivity of carbamate. But in the case of aromatic primary amine, the crystalline product formed on analysis was found to be biphenyl urea (BPU).

The effect of the molar ratio of amine to DMC was investigated in a reaction between n-butyl amine and DMC. It is clear from **Fig. 6** which the percentage conversion of n-butyl amine increased with an increase in the amount of DMC up to a molar ratio of 1: 7. The excess quantity of DMC might be useful as a solvent and also to promote lower steric interaction of amine molecules. Then it helps to activate the amine molecules by the polarized carbonyl group of DMC which are lodged over the acid sites of the catalysts. The effect of temperature on catalytic activity and the optimum temperature of the reaction was found to be 348 K (**Fig. 7**). It is evidenced from **Fig. 6** at lower temperatures, conversion of the amine was lower, whereas at higher temperatures, the selectivity of carbamate decreased due to the formation of N-methylated amine. The effect of reaction time on the conversion of amine is investigated

for 1-12 hour. It is observed from **Fig. 8** that the % conversion of amine increased with the duration of reaction and complete conversion of 1-butyl amine was observed after 12 hours.

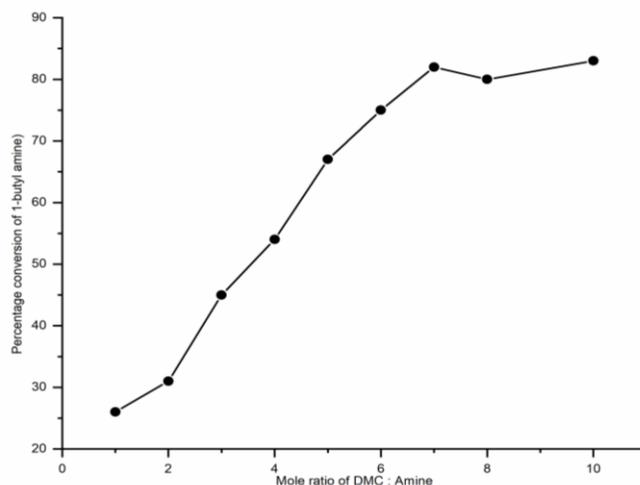


Fig. 6. Effect of mole ratio of DMC to amine on the catalytic activity

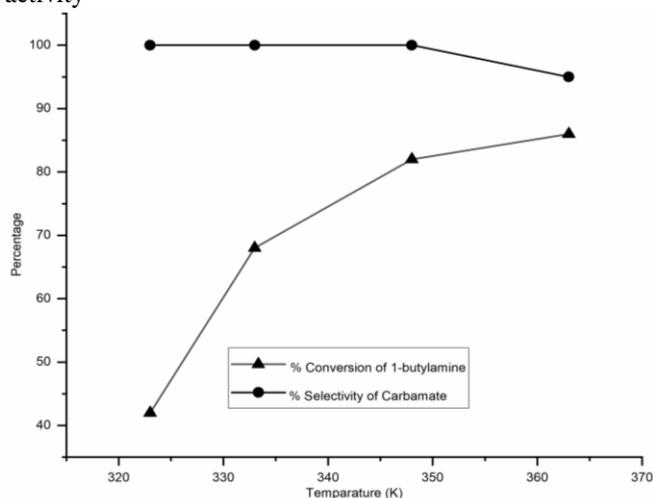


Fig. 7. Effect of reaction temperature on the catalytic performance.

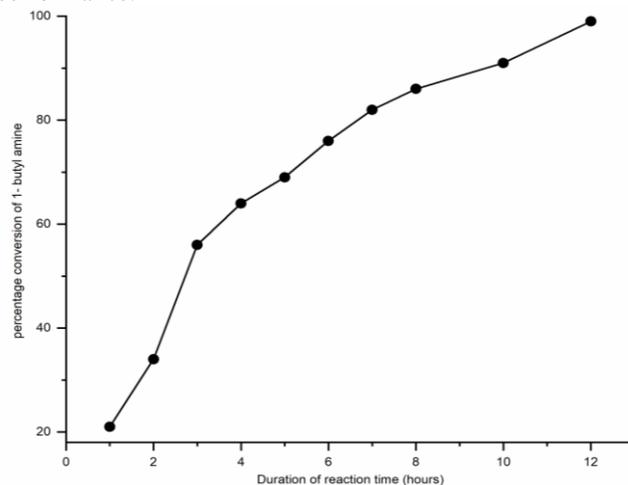


Fig. 8. Effect of reaction duration on the conversion of 1-butylamine

Table 3. Catalytic activity of Zinc Aluminophosphate for the synthesis carbamates using different types of amines

Amine	Reaction temperature (K)	% amine conversion	%selectivity towards carbamate	% Yield of carbamate
1-Butyl amine	348	82	100	69
Cyclohexylamine	358	51	100	38
1,6-Hexamethylene diamine	358	73	91	60
Aniline	440	54	31	23
Di-tert-butylamine	385	Nil	-	-

3.5. Reusability of the catalyst

The reusability of catalyst ZnAIP5 was tested five times and found that the conversion and selectivity of the catalysts remain almost the same throughout all the cycles. The observations are indicated in **Fig. 9**. The slight changes observed in terms of activity might be due to the physical loss of the catalyst during separation. After each cycle, the catalyst in the reaction mixture was separated by filtration. The filtered catalyst is stirred in acetone for 15 minutes to remove the organic compounds and the sample was dried slowly to 250 °C.

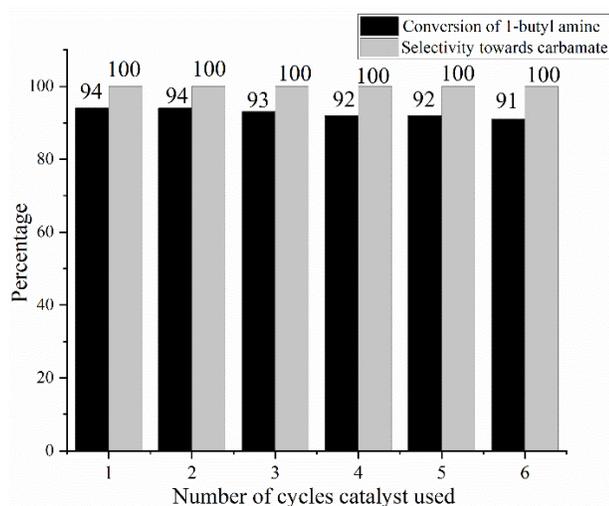


Fig. 9. Reusability of ZnAIP5 catalyst in the methoxycarbonylation reaction of 1-butylamine

4. Conclusions

Amorphous metal phosphates and metal aluminophosphates are prepared by a simple co-precipitation method in the absence of templating agents. Materials are characterized to understand their physico-chemical properties using various techniques. The incorporation of Cu or Zn into AIP during precipitation plays a major role in determining the surface and acid properties of aluminophosphate. These materials are applied as a solid heterogeneous catalyst for phosgene free synthesis of industrially important carbamates from amines and environmentally benign

DMC. ZnAIP5 is found to be an excellent catalyst for the synthesis of carbamates due to its moderate acidity. The incorporation of Zn to aluminophosphate plays an important role in the structural and surface properties of ZnAIP. Reaction conditions are optimized, and reusability of the catalyst is studied to obtain a better yield using an efficient catalyst through ecofriendly method.

Acknowledgements

We thank St Josephs college, Bangalore for the PXRD facility.

References

- [1]. N. Germain, I. Muller, M. Hanauer, R. A. Paciello, R. Baumann, O. Trapp, and T. Schaub, *ChemSusChem*. 9 (2016) 1-6.
- [2]. K. J. Dorweiler, J. N. Guray, J. S. Walbridge, V. S. Ghatge, R. H. Savant, *J. Agric. Food Chem.* 64 (2016) 6108–6124.
- [3]. E. Sawatzky, S. Wehle, B. Kling, J. Wendrich, G. Bringmann, C. A. Sotriffer, J. Heilmann, M. Decker, *M. J. Med. Chem.* 59 (2016) 2067–2082.
- [4]. S. Shahsavari, C. McNamara, M. Sylvester, E. Bromley, S. Joslin, B. Lu and S. Fang, *Beilstein J. Org. Chem.* 14 (2018) 1750–1757.
- [5]. E. Reixach, R. M. Haak, S. Wershofen and A. V. Ferran, *Ind. Eng. Chem. Res.* 51 (2012) 16165–16170.
- [6]. D. Zhan, Y. Zhang, Y. Fan, M. N. Rager, V. Guerineau, L. Bouteiller M. Li and C. M. Thomas, *Macromolecules* 52 (2019) 2719–2724.
- [7]. O. Kreye, H. Mutlu, M. A. R. Meier, *Green Chem.* 15 (2013) 1431-1455.
- [8]. A. K. Ghosh, M. Brindisi, and A. Sarkar, *ChemMedChem*. 13 (2018) 2351-2373.
- [9]. J. V. P. Katuria, K. Nagarajan, *Tetrahedron Let.* 60 (2019) 552-556.
- [10]. T. Mikael, A. Jerome, Nahla, T. Isabelle, R. Brigitte, P. Sebastien, *Org. Biomol. Chem.* 17 (2019) 5420-5427.
- [11]. X. Peng, F. Li, X. Hu, C. Xia, C. A. Sandoval, *Chin. J. of Catal.* 29 (2008) 638-642.
- [12]. A. V. Tran, T. T. Nguyen, H. J. Lee, S. W. Bae, J. Baek, H. S. Kim, Y. J. Kim, J. Shang, X. Guo, F. Shi, Y. Ma, F. Zhou, Y. J. Deng, *App. Catal. A. Gen.* 587 (2019) 117245-117300.
- [13]. Q. Sun, R. Niu, H. Wang, B. Lu, J. Zhao, Q. Cai, *Micropor. Mesopor. Mat.* 248 (2017) 108-114.

- [14]. Q. Zhang, H. Yuan, X. Lin, N. Fukaya, T. Fujitani, K. Sato and J. Choi, *Green Chem.* 22 (2020) 4231-4239.
- [15]. B. Puertolas, M. Rellan-Pineiro, J. L.N. Rico, A. P. Amrute, A. V. Ferran, N. Lopez, J. P. Ramirez, S. Wershofen, *ACS Catal.* 9 (2019) 7708–7720.
- [16]. V. Acharya, S. Mal, J. P. Kilaru, M. G. Montgomery, S. H. Deshpande, R. P. Sonawane, B. N. Manjunath, and S. Pal, *Eur. J. Org. Chem.* 3 (2020) 378-387.
- [17]. Q. Zhang, H. Yuan, N. Fukaya, and J. Choi, *ACS Sustainable Chem. Eng.* 6 (2018) 6675-6681.
- [18]. I. D. Inaloo, S. Majnooni, *ChemistrySelect* 4 (2019) 7811-7817.
- [19]. N. Germain, M. Hermsen, T. Schaub and O. Trapp, *Appl Organometal Chem.* 31 (2017) 3733.
- [20]. H. Y. Yuan, Q. Zhang, N. Fukaya, X. T. Lin, T. Fujitani, and J. C. Choi, *Bullet. Chem. Soc. Japan* 91 (2018) 1481-1486.
- [21]. I. D. Inaloo, S. Majnooni, *New J. Chem.* 43 (2019) 11275-11281.
- [22]. Q. Zhang, H. Y. Yuan, N. Fukaya, H. Yasuda, J. C. Choi, *ChemSusChem.* 10 (2017) 1501-1508.
- [23]. H. Q. Li, Y. Cao, X. T. Li, L. G. Wang, F. J. Li, G. Y. Zhu, *Ind. Eng. Chem. Res.* 53 (2014) 626-634.
- [24]. D. L. Sun, J. Y. Luo, R. Y. Wen, J. R. Deng, Z. S. Chao, *J. Haz Mat.* 266 (2014) 167-173.
- [25]. S. R. Buzo, Sergio, P. G. Garcia, A. Corma, *Catal. Sci. Technol.* 9 (2019) 146-156.
- [26]. A. Hamza, N. Nagaraju, *Chin. J. Catal.* 36 (2015) 209-215.
- [27]. A.V. Vijayasankar, S. Govindaraju, *Chem. Data Collect.* 28 (2020) 100419.
- [28]. A. V. Vijayasankar, N. Mahadevaiah, Y.S. Bhat, N. Nagaraju, *J. Porous. Mater.* 18 (2011) 369-378.
- [29]. N. Nagaraju, G. Kuriakose, *Green Chem.* 4 (2002) 269-271.
- [30]. J. B. Moffat, *Catal. Rev.* 18 (1978) 199-258.
- [31]. R. Rosseto, A. C. M. A. Dos Santos, F. Galembeck, *J. Braz. Chem. Soc.* 17 (2006) 1465-1472.
- [32]. A. Whitaker, *Acta. Crystallogr. Sec. B*, 31 (1975) 2026-2035.
- [33]. K. S. W. Sing, *Pure and Appl. Chem.* 54 (1982) 2201-2218.
- [34]. G. Liu, Z. Wang, M. Jia, X. Zou, X. Zhu, W. Zhang, D. Jiang, *J. Phys. Chem. B.* 110 (2006) 16953-16960.
- [35]. A. M. Márquez, J. Oviedo, J. F. Sanz, J. J. Benítez, J. A. Odriozola, *J. Phys. Chem. B.* 101 (1997) 9510-9516.
- [36]. S. Grego, F. Aricò and P. Tundo, *Org. Process Res. Dev.* 17 (2013) 679–683.
- [37]. B. Wang, J. He, R. C. Sun, *Chin. Chem. Lett.* 21 (2010) 794-797.
- [38]. M. Litwinowicz and J. Kijeński, *Sustain. Chem. Processes* 3 (2015) 1-7.
- [39]. M. Kang, H. Zhou, B. Qin, C. Han, D. Tang, J. Shang, and N. Zhao, *ACS Omega* 5 (2020) 22529-22535.
- [40]. M. Busio, J. Janchen, J. H. C. Van Hoff, *Micropor. Mesopor. Mater.* 5 (1995) 211-218.
- [41]. R. Mokaya, W. Jones, Z. Luan, M. D. Alba, J. Klinowski, *Catal. Lett.* 37 (1996) 113-120.