*Science in China Series B: Chemistry*



Springer

www.scichina.com
chem.scichina.com
www.springerlink.com

# Database of open-framework aluminophosphate syntheses: introduction and application (Ⅰ)

YAN Yan[1], LI JiYang[1], QI Miao[2], ZHANG Xiao[1], YU JiHong[1†] & XU RuRen[1†]

[1] State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, Jilin University, Changchun 130012, China;
[2] Department of Chemistry, Northeast Normal University, Changchun 130117, China

**The database of open-framework aluminophosphate (AlPO) syntheses has been established, which includes about 1600 synthetic records. Data analysis has been done on the basis of the framework composition, structure dimension, pore ring, and organic template. This database will serve as useful guidance for the rational synthesis of microporous functional materials.**

aluminophosphates, open framework, synthesis, database

## 1 Introduction

Open-framework aluminophosphates (AlPOs) constitute an important family of zeolites and related microporous materials since the first discovery of aluminophosphate molecular sieves $AlPO_4$-*n* in 1982 by U.C.C.[1]. $AlPO_4$-*n* is made of the strict alternation of $AlO_4$ and $PO_4$ tetrahedra through corner sharing to form a neutral framework with Al/P=1[2]. Microporous aluminophosphates have aroused wide interest because of their rich structural chemistry and potential applications in catalysis, adsorption and assembly[3,4]. Great progress has been made in the synthesis of open-framework aluminophosphates during the past 20 years. So far, more than 60 kinds of aluminophosphate molecular sieves have been successfully synthesized. Notable examples are VFI with extra-large 18-ring channels[5] and JRY with 10-ring chiral channels[6]. Besides, a large number of aluminophosphates with anionic frameworks have been prepared with zero dimensional (0-D) clusters, 1-D chains, 2-D layers and 3-D open-frameworks. Their Al/P ratios are found as 1/1, 1/2, 2/3, 3/4, 4/5, 5/6, 6/7, 11/12 and 12/13 and so forth[7,8]. Notable examples include JDF-20 with the largest 20-ring channel[9], and AlPO-CJB1 with Brönsted acidic center[10].

Recently, the rational synthesis of new materials has become significantly important in the field of materials chemistry. However, the designed synthesis of microporous materials is of great challenge because of unclear crystallization mechanism under hydrothermal or solvothermal conditions[11,12]. Our research group has been making continuous efforts on the designed synthesis of microporous materials. For example, we developed some computational methods for the design of zeolite structures with specified channels[13−15] and AlPO structures with special Al/P ratios[16] as well as methods for the design of extra-large pore open-framework structures in terms of the concept of scale-chemistry[17]. We also explored the template-directed approach to the synthesis of the open-framework materials based on the host-guest interactions[18−20]. However, the crystallization kinetics of such materials is rather complex. A better understanding of the relationship between the synthetic factors and the resulting structures is of crucial importance to rationalize the synthesis of the target microporous materials. Therefore, we have built up a database of AlPO syntheses[21] containing detailed synthesis information of

Received July 17, 2009; accepted August 19, 2009
doi: 10.1007/s11426-009-0266-x
†Corresponding author (email: jihong@jlu.edu.cn, rrxu@jlu.edu.cn)
Supported by the National Natural Science Foundation of China (Grant No. 20871051), the State Basic Research Project of China (2006CB806103) and the Major International Joint Research Project of China (20720102039)

open-framework AlPOs reported in the literature, as well as some experimental data from our research group. We aim to discover the relationship between the synthetic features and specific structural features of microporous materials through data mining techniques. Now the database is available at the IZA website of http://www.iza-structures.org/database/[22]. This article will introduce the database of open-framework aluminophosphate (AlPO) syntheses. The construction of this database will lay an important foundation for the rational design and synthesis of microporous materials.

## 2 Experimental section

The database system is running on Linux, and the web server is built up with Apache/2.2.8+(Linux)PHP5.2.5. The web page scripts were written by computer language PHP5.2.5. MySQL 4.1.7-Standard was used as the database management system. NotePad++ was used as PHP editor to design the interface.

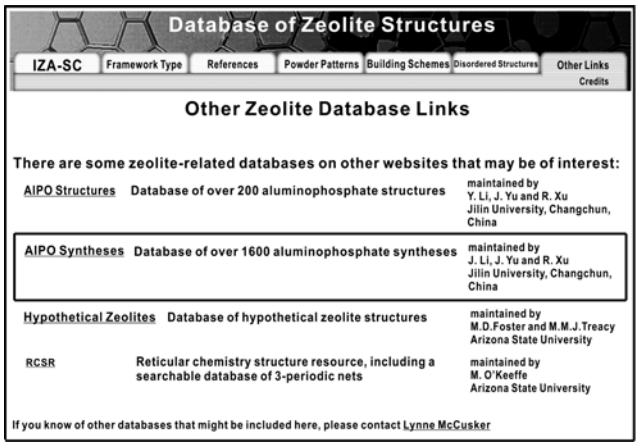
## 3 Results and discussion

### 3.1 Construction and function of the database

3.1.1 System framework. MVC (Model, View and Controller) model was adopted to design the framework of the website. The aim is to realize the function division of the web system, which in practice means introducing hierarchy in design. The functions of the whole website system can be divided into the following modules: data access layer (including entities and associations), data operation layer (including views and view connection), program service layer (including application modules), and client visit layer (including the format and style of web pages in browsers). The framework of the database is described in Scheme 1.

3.1.2 Design of the database. MySQL was used as the database management system. The information of database has been stored in 5 different datasheets including reference, source materials, batch composition, crystallization condition and product.

3.1.3 Design of the interface of the database. To ensure the enduring stability of the database of AlPO syntheses, the whole interface is designed by NotePad++ editor, in which PHP script can be encoded directly. Currently, the database has been linked to the International Zeolite Association (IZA) website for free use (Figure 1). The Database of AlPO syntheses includes three parts (Figure 2): Introduction, Data Search and Search Help. The Introduction part simply introduces the general website. The Search section is the core of the database. The Search Help section elucidates the detailed search rules.




**Scheme 1** The framework of the database of AlPO syntheses.




**Figure 1** Database of AlPO syntheses at the IZA website.


**Figure 2** Interface of the AlPO Database.

3.1.4 Search function of the database. Each record in the synthesis database comprises the detailed information about reference, source materials, template used in the synthesis, synthetic condition, and structural characters of the product. Quick and advanced searches are available for many items in the database (Figure 3), such as ring number, framework composition, source material, template, crystallization time, crystallization temperature, etc. The Database of AlPO syntheses has a strong data extraction capability. It will help the user to find the required data quickly. The search result can be displayed according to the sort of the literature, ID number and so forth. One can view detailed information in the literature by clicking the ID number or title of the reference. Figure 4 gives a research example of $AlPO_4$-5.

### 3.2 Data analysis and statistics

The synthesis database contains 1585 reaction data relevant to over 230 kinds of AlPO structure types. The data are mainly collected from journals, proceedings, patents, and some experimental data of our group. The database of AlPO syntheses is updated continually, which will provide the most latest synthetic data of AlPOs for users.

Some statistical analyses of the syntheses data have been done in the following aspects.

3.2.1 Pore rings. Pore size is a key factor to describe the pore structure of open-framework aluminophosphates. The pore rings are usually defined as the number of T atoms (T = Al or P) that enclose the pore window. In the database of open-framework aluminophosphate (AlPO) syntheses, the products can be classified according to the pore rings, such as extra-large pores (>14-rings), large pores (12-rings), medium pores (10-rings) and small pores (8-rings). Figure 5 shows the classification results. There are 63 records for the extra-large pore aluminophosphates, accounting for 4.60% of the total data, and 448 records for large pore aluminophosphates, corresponding to 27.98% of the total data. The synthesis records of medium and small pore aluminophosphates are 9.43% and 35.80% of the total data, respectively. Other low-dimensional aluminophosphates occupy 22.11%.

3.2.2 Framework compositions. $AlPO_4$-*n* is made up of alternation of $AlO_n$ ($n$ = 4,5,6) and $PO_4$ units. The lattice Al or P atoms can be partially replaced by silicon or other elements to yield SAPO (S = Si) and MAPO (M = metal ion) open-framework structures with special properties. The collected data in the synthesis database display rich framework compositions (Figure 6). There are 823 records associated with pure AlPO compounds, occupying 51.92% of the data. Some other elements, such as Si, Co, Mn, Mg, V, etc., incorporating into the framework of AlPOs, can also be found. There are 242 records

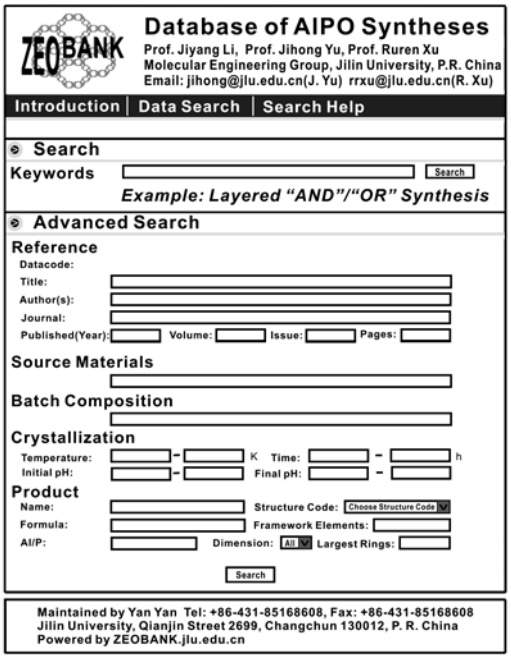



**Figure 3** Search interface of the database.


**Figure 4** The research result of aluminophosphate $AlPO_4$-5.

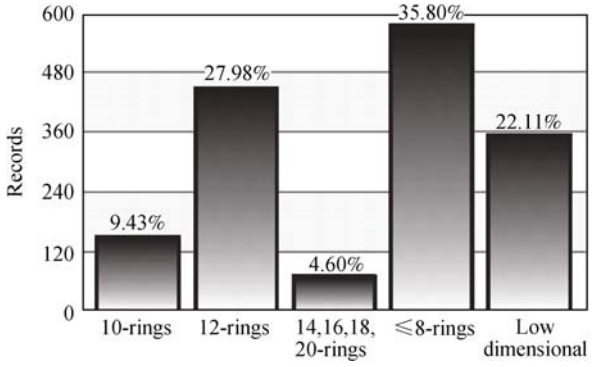



**Figure 5** Distribution of the synthetic data according to the pore rings.

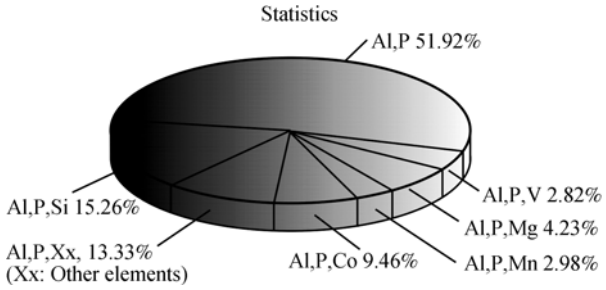



**Figure 6** Distribution of the synthetic data of various framework compositions in the synthesis database.

for SAPO (15.26%), 150 records for CoAPO (9.46% ), 47 records for MnAPO (2.98% ), 67 records for MgAPO (4.23% ), and 33 records for VAPO (2.82%).

3.2.3 Framework dimensions of the products. The aluminophosphates collected in the database exhibit various framework architectures including zero-dimensional (0-D) clusters, 1-D chains, 2-D layers and 3-D open frameworks. Currently the database contains 1585 data (71.57%) for 3-D open frameworks, 12.32% for 2-D layers, 3.98% for 1-D chains, 12.13% for 0-D clusters. Figure 7 shows the distribution of the framework dimensions of AlPOs in the database.

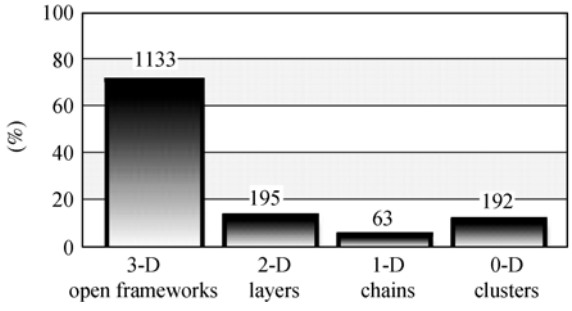



**Figure 7** Distribution of the synthetic data of various framework dimensions of AlPOs in the synthesis database.

3.2.4 Organic templates. The organic template plays a dominant role in determining the formation of a specific framework of microporous materials. Different organic templates can direct different products under similar synthetic conditions. Therefore, studies of the relationship between the organic template and the final product will be very important.

Over 100 kinds of organic templates have been collected in the database, including mono-amines, di-amines, poly-amines, cyclo amines, and so on. There exist 48 records for methylamine as the template, and 97 records for ethylenediamine as the template. For the polyamines, diethylenetriamine and triethylenetetramine are the most commonly used ones with records of 56 and 42, respectively.

Three relationships have been found between the organic templates and the inorganic open frameworks: i) one template-multiple structures, ii) multiple templates-one structure, iii) One template-one structure. The first two phenomena are remarkable in the synthesis of open-framework AlPOs. For example, di-*n*-propylamine ($Pr_2NH$) has been used in the synthesis of nine different AlPO structures as seen in Table 1. On the other hand, one structure can be synthesized by many different templates. For instance, $AlPO_4$-5 is much less template specific that can be synthesized with a number of different templates in the records. Tetrapropylammonium hydroxide is a typical template for the synthesis of $AlPO_4$-5. Moreover, a number of organic amines can also direct the synthesis of $AlPO_4$-5 molecular sieves, such as tripropylamine(TrPA), triethylamine(TrEA), diethylenetriamine, tetramethylammonium, *N,N*-dimethylethanolamine, tetrapropylammonium, dicyclohexylamine, cyclohexylamine, 2-methylpyridine, hexahydropyridine, triethanolamine, 8-hydroxyquinoline, *N*-methylcyclohexanamine, diethanolamine, tri-*n*-butylamine, diethylamine, 1,4-diazabicyclo-[2.2.2] octane, hexamethylenetetramine, methylamine, etc.

A few AlPO structures exhibit high template specificity. For example, there are 4 records associated with $AlPO_4$-20, all of which involve TMAOH as the template. In addition, triethylamine is the only used template in the 20 synthetic records for JDF-20.

In the synthesis of AlPOs, two templates sometimes appear to cooperatively direct the formation of a structure. For instance, SAPO-37 is prepared in the presence of a mixture of TPAOH and TMAOH.

**Table 1** The statistics of synthetic records by using dipropylamine ($Pr_2NH$) as the template

| Code | Batch composition | Product | Structure code | Record (s) |
|---|---|---|---|---|
| 1 | {1.80-2.20}$Pr_2NH$:{0.30}MgO:{0.85}$Al_2O_3$:{1.0}$P_2O_5$:{50}$H_2O$ | MAPO-46(A-F) | AFS | 6 |
| 2 | $Al_2O_3$:$P_2O_5$:$TiO_2$:i-$Pr_2NH$:$H_2O_2$:$C_6H_{14}O_4$ | TiAPO-41 | AFO | 1 |
| 3 | {0.5}$Al_2O_3$:{1.0}$P_2O_5$:{2.0}$Pr_2NH$:{48}$H_2O$ | AlPO-41 | AFO | 1 |
| 4 | {1.0}$Al_2O_3$:{1.0}$P_2O_5$:{1.0}$Pr_2NH$:{80}$H_2O$ | VPI-5 | VFI | 1 |
| 5 | {1.0}$Al_2O_3$:{1.0}$P_2O_5$:{1.0}$Pr_2NH$:{70}$H_2O$ | $AlPO_4$-11 | AEL | 1 |
| 6 | {1.0}$Al_2O_3$:{1.0}$P_2O_5$:{0.6}$SiO_2$:{1.0}$(TEA)_2O$:{0.5}$Pr_2NH$:{50}$H_2O$ | SAPO-34 | CHA | 1 |
| | {1.0}$Al_2O_3$:{1.2}$P_2O_5$:{0.3}$SiO_2$:{0.5}$(TEA)_2O$:{1.6}$Pr_2NH$:{52}$H_2O$ | SAPO-34 | CHA | 1 |
| 7 | {1}$Al_2O_3$:{1}$P_2O_5$:{0.3}$SiO_2$:{1}$Pr_2NH$:{50}$H_2O$ | SAPO-31 | ATO | 1 |
| | {1}$Al_2O_3$:{1}$P_2O_5$:{0.3}$SiO_2$:{1}$Pr_2NH$:{30}$H_2O$ | SAPO-31 | ATO | 1 |
| 8 | {1}$Al_2O_3$:{1.0-1.3}$P_2O_5$:{0.1-0.6}$SiO_2$:{2.0-4.0}$Pr_2NH$:{60}$H_2O$ | SAPO-46 | AFS | 1 |
| 9 | {0.9}$Al_2O_3$:{0.85}$P_2O_5$:{0.3}$SiO_2$:{0.2}CoO:{2}$Pr_2NH$:{55}$H_2O$ | CoSAPO-46 | AFS | 1 |

## 4 Conclusions

The database of open-framework aluminophosphate (AlPO) syntheses has been established based on Linux platform by using PHP + Apache + MySQL framework. The database contains about 1600 reaction data. This database has search, analysis and statistic functions. Our further work will focus on the use of data-mining techniques to derive useful information about synthetic conditions and resulting structures, which can be used to guide the rational synthesis of microporous materials. We believe that with the improvements of the quality of the synthesis database and the data mining techniques, we will open up a new route for the rational synthesis of inorganic crystalline materials


1 Wilson S T, Lok B M, Messina C A, Cannan T R, Flanigen E M. Aluminophosphate molecular sieves: a new class of microporous crystalline inorganic solids. J Am Chem Soc, 1982, 104(4): 1146－1147
2 Bennett J M, Dyttych W J, Pluth J J. Structural features of aluminophosphate materials with Al/P＝1. Zeolites, 1986, 6(9): 349－360
3 Yu J H, Xu R R. Insight into the construction of open-framework aluminophosphates. Chem Soc Rev, 2006, 35(7): 593－604
4 Thomas J M, Raja R, Sankar G, Bell R G. Molecular-sieve catalysts for the selective oxidation of linear alkanes by molecular oxygen. Nature, 1999, 398: 227－230
5 Davis M E, Saldarriaga C, Montes C, Garces J, Crowder C. A molecular sieve with eighteen-membered rings. Nature, 1988, 331, 698－699
6 Song X W, Li Y, Gan L, Wang Z P, Yu J H, Xu R R. Heteroatom-stabilized chiral framework of aluminophosphate molecular sieves. Angew Chem Int Ed, 2009, 48(2): 314－317
7 Yu J H, Xu R R. Rich structure chemistry in the aluminophosphate family. Acc Chem Res, 2003, 36(7): 481－490
8 Xing H Z, Li J Y, Yan W F, Chen P, Jin Z, Yu J H, Dai S, Xu R R. Cotemplating ionothermal synthesis of a new open-framework aluminophosphate with unique Al/P ratio of 6/7. Chem Mater, 2008, 20: 4179－4181
9 Huo Q S, Xu R R, Li S G, Ma Z G, Thomas J M, Jones R H, Chippindale A M. Synthesis and characterization of a novel extra large ring of aluminophosphate JDF-20. J Chem Soc, Chem Commun, 1992, 875－876
10 Yan W F, Yu J H, Xu R R, Zhu G S, Xiao F S, Han Y, Kazumasa S, Osamu T. $[Al_{12}P_{13}O_{52}]^{3-}[(CH_2)_6N_4H_3]^{3+}$: An Anionic aluminophosphate molecular sieve with Brönsted acidity. Chem Mater, 2000, 12(9): 2517－2519
11 Yu J H, Xu R R. Toward the rational design and synthesis of inorganic microporous and related materials. Stud Surf Sci Catal, 2004, 154: 1－13
12 Corma A. Towards a rationalization of zeolite and zeolitic materials synthesis. Stud Surf Sci Catal, 2004, 154: 25－40
13 Li Y, Yu J H, Liu D H, Yan W F, Xu R R, Xu Y. Design of zeolite frameworks with defined pore geometry through constrained assembly of atoms. Chem Mater, 2003, 15: 2780－2785
14 Li Y, Yu J H, Wang Z P, Zhang J N, Guo M, Xu R R. Design of chiral zeolite frameworks with specified channels through constrained assembly of atoms. Chem Mater, 2005, 17: 4399－4405
15 Li Y, Yu J H, Xu R R, Baerlocher C, McCusker L B. Combining structure modeling and electron microscopy to determine complex zeolite framework structures. Angew Chem Int Ed, 2008, 47: 4401－4405
16 Li Y, Yu J H, Jiang J X, Wang Z P, Zhang J N, Xu R R. Prediction of open-framework aluminophosphate structures using the automated assembly of secondary building units method with Lowenstein's constraints. Chem Mater, 2005, 17: 6086－6093
17 Ren X Y, Li Y, Pan Q H, Yu J H, Xu R R, Xu Y. A crystalline germanate with mesoporous 30-ring channels. J Am Chem Soc, 2009, 131(40): 14128－14129
18 Li J Y, Li L, Liang J, Chen P, Yu J H, Xu Y, Xu R R. Template-designed syntheses of open-framework zinc phosphites with extra-large 24-ring channels. Cryst Growth Des, 2008, 8(7): 2318－2323
19 Li J Y, Yu J H, Yan W F, Xu Y H, Xu W G, Qiu S L, Xu R R. Structures and templating effect in the formation of 2D layered aluminophosphates with $Al_3P_4O16^{3-}$ stoichiometry. Chem Mater, 1999, 11: 2600－2606
20 Yu J H, Li J Y, Wang K X, Xu R R, Sugiyama K, Terasaki O. Rational synthesis of microporous aluminophosphates with an inorganic open framework analogous to $Al_4P_5O_{20}H{\cdot}C_6H_{18}N_2$. Chem Mater, 2000, 12: 3783－3787
21 Li J Y, Yu J H, Xu R R. Database of AlPO Syntheses: http://zeobank.jlu.edu.cn
22 Baerlocher Ch, McCusker L B. Database of zeolite structures: http://www.iza-structures.org/database/