Ionothermal Synthesis of Metal Aluminophosphates

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Abstract

The aim of this thesis was to synthesise CoAPO-34 and FeAPO-34 using ionothermal synthesis in the presence of organic amines. Using this method provides an alternative route to prepare such materials under low pressure instead of the higher pressure associated with hydrothermal or solvothermal synthesis. Both materials have chabazite (CHA) topology and they are known to act as catalysts.

CoAPO-34 was ionothermally prepared using 1-ethyl-3-methylimidazolium bromide (EMIMBr) in presence of 1, 6-hexadiamine (HDA). This study has found that when the synthesis was carried out without HDA, AlPO-11 was preferentially obtained instead of CoAPO-34. Broad line signals which appear between 2000 to 5000 ppm in both spin-echo ^{31}P NMR spectra of as-synthesised and calcined CoAPO-34 confirm that the Co^{2+} ions have been successfully incorporated within the framework of the material.

FeAPO-34 was synthesised under ionothermal conditions using 1-ethyl-3-methylimidazolium chloride in the presence of ethylenediamine (EDA). In the absence of EDA, the synthesis has produced AlPO-34 instead of FeAPO-34. Broad line signals that appear between 1000 to 14000 ppm in spin-echo ^{31}P NMR spectra of both as-synthesised and calcined FeAPO-34 are direct evidence of isomorphous substitution of framework aluminum by Fe(II) or Fe(III).

Another aim of this study was to explore the ionothermal synthesis of copper containing aluminophoshate of DNL-1 (Cu/DNL-1). This material was attractive to explore because it contains 20 ring extra-large pores and Cu(I) species in the channels of the framework, potentially giving material the ability to simultaneous store NO and to generate NO from NO_2^- anions.

Cu/DNL-1 was successfully prepared under ionothermal conditions using EMIMBr and HDA. Without HDA in the synthesis, AlPO-11 was obtained. In this material, copper ions were not incorporated in the Cu/DNL-1 skeleton framework. This was confirmed by absence of broadline signal at >500 ppm in spin-echo ^{31}P NMR spectrum of the sample. The copper ions are expected to be present as extra-framework cations. Extra-framework Cu(I) species that were formed by high temperature calcination of Cu/DNL-1 are active to produce NO from NO_2^-. Therefore, the calcined Cu/DNL-1 can be used to simultaneously store and produce NO from nitrite. This has the potential to significantly extend the lifetime of gas delivery in the material to prevent thrombus formation.

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CHAPTER 1

INTRODUCTION

1.1: Zeolites

Zeolite based molecular sieves are a vital inorganic material group in industrial application used as ion exchangers, catalysts and adsorbents.[1] These porous material have been known almost 250 years as crystalline aluminosilicates constructed from corner -sharing TO_4 tetrahedra (T = silicon or aluminium atom) T= Al/P are also common, although they are not strictly zeolites .[2] The general formula of aluminosilicate zeolite can be represented as follows:

$$M_{y/z}[(SiO_2)_x.(AlO_2)_y].qH_2O$$

Where **x** and **y** are integer for equal or greater than 1, **M** is cation and **q** is the number of water molecules in each unit cell.[3]

Zeolites are important in catalysis because of the formation of BrØnsted acid sites (shown in Figure 1.1). Every time an Al replaces a Si in the structure; a negative charge is produced, which must be balanced by cation. This can be a proton (H^+) as shown in Figure 1.1, or other cations such as Na^+, Ca^{2+} and etc.[2]

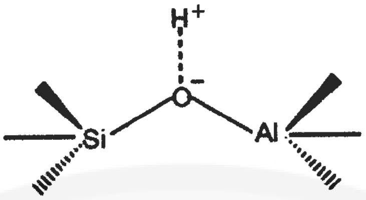

Figure1.1 Basic chemical structure of the BrØnsted acid site zeolite aluminosilicate [4]

The history of zeolites began in 1756 when the Swedish mineralogist Axel Fredrick Cronstedt observed the rapid heating of stilbite, which produced large amounts of steam from the mineral that absorbed water. He named the stone zeolite from the Greek words 'zeo' meaning 'boil' and 'lithos' is 'stone'.[2] Since then, approximately 40 natural zeolite frameworks[2] and 213 unique structures are identified.[5]

Natural zeolites are formed when the volcanic rocks (solidified lava) and ash layers crystalized under reaction with alkaline/ saline lake or ground water.[6] The most common natural zeolites are chabazite, offretite, faujasite and mordenite.[3] Naturally occurring zeolites are contaminated by various degrees of metals, minerals, quartz and other zeolites. Owing to this natural zeolites are often excluded from many essential commercial applications where purity and uniformity are accentuated. However, natural zeolites are often preferred for use in environmental application where they can be employed in the simpler manner where the raw material just crushed into the powder. Zeolites are also used in widespread application as a filler in cement, in paper, in fertilizer and soil conditioner and as dietary supplements in animal husbandry.[6]

Synthetic zeolites were first made by Barrer in late 1940 using higher temperature and pressure to synthesis of modernite. The discovery inspired Milton (1959) and Breck (1964) to synthesis zeolite A, X and Y under milder condition using much lower temperature and pressure than earlier. In 1954 a number of synthetic zeolites were introduced by Union Carbide as new industrial materials for separation and purification process.[7] Many of new synthetic zeolites with no natural counterpart have larger pores size and higher volume capacity rather than most known natural zeolites. Zeolites with larger pore size have advantages in that larger molecules can be used as reactants.[8]

Zeolite frameworks are based on individual tetrahedral unit (TO_4) called a 'Primary building unit (PBU). The PBUs are link together to form secondary building units (SBUs) which consist of n-ring structure. Figure 1.2 shows 20 kinds of SBUs that have been found in tetrahedral frameworks.[9] Each corner in SBUs represent T atoms belonging to TO_4 where oxygen (not plotted for clarity) are found near at the middle of the lines joining each pair of T.

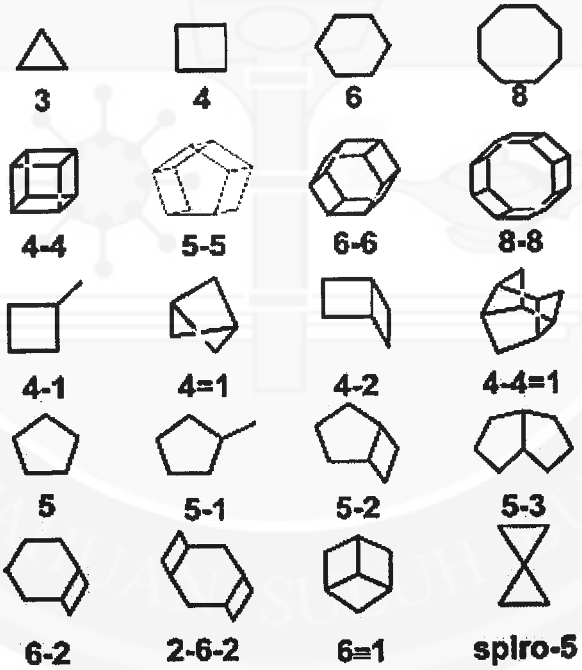

Figure 1.2: Secondary building units (SBUs) and their symbols [9]

SBUs can be linked to form 'tertiary building units' (TBUs). Further connecting TBUs generate large polyhedral building block to form a characteristic pore system. Figure 1.3 shows an example, where the β-cage (sodalite cage) is built by six 4-rings and eight 6-rings. It is a common unit joined together in different arrangements to produce a variety of frameworks e.g SOD, LTA, EMT and FAU.[10] The structure Commission of the International Zeolite Association (IZA-SC) has assigned the three letter codes to all unique frameworks of zeolite topologies.[2]

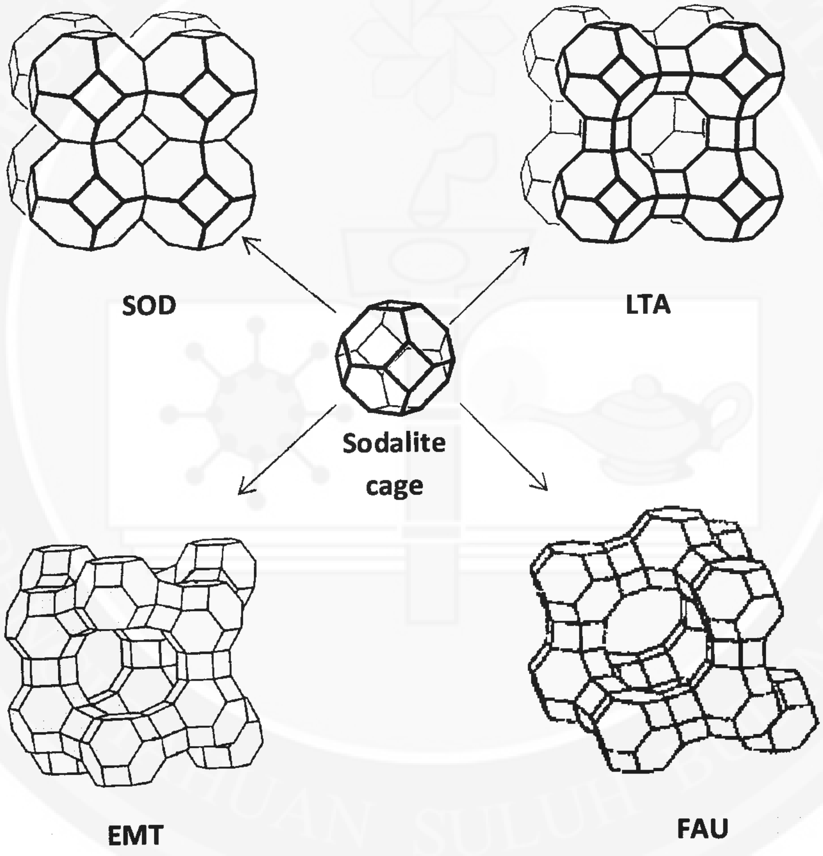

Figure 1.3: Schematic of Sodalite cage frameworks [11]

1.2: Applications of zeolites

Zeolites have unique properties including good thermal stability, acidity, ion-exchange capacity, uniform molecular sized channels, adsorption for gas or vapor and catalytic properties. Owing to these properties, zeolites are used widely in many applications such as environmental treatment, laundry detergents, oil refining and petrochemical industries, adsorption, gas separation, agriculture and horticulture.[12] Generally, the main uses of zeolites can be categorized into three functional classifications: ion exchange, catalysis and adsorption-separation.

1.2.1: Ion exchange applications

Cation exchange properties of traditional aluminosilicate zeolites arise from the isomorphous positioning of aluminium in tetrahedral coordination within their Si/Al frameworks. This imposes a net negative charge on the framework counterbalanced by cations held within the cavities and channels. This is said to create facile cation exchange "lubricated" by the water molecules also present in the voids within the framework. This certainly is the case for zeolites with open frameworks but in the more narrow-pored frameworks, such as natrolite, cation replacement is slow and difficult.[13]

Cation exchange is exploited in water softening, where alkali metals such as Na^+ or K^+ in zeolite framework are replaced by Ca^{2+} and Mg^{2+} ions from water. Many commercial washing powders thus contain substantial amounts of zeolites that enhance washing efficiency. LTA is the subject of the largest scale production of synthetic zeolites for use as "builders" in domestic and commercial detergents to remove the calcium and magnesium "hardness".[14]

The unique ion exchange properties of zeolites can also be used for cleaning up of commercial waste water containing heavy metals and nuclear effluents containing radioactive isotopes. In a similar way zeolites can absorb ions and molecules and thus act as a filter for odor control and toxin removal.[13]

1.2.2: Adsorption and separation applications

The shape-selective properties of zeolites are the basis for their use in molecular adsorption and separation. The ability preferentially to adsorb certain molecules, while excluding others, has opened up a wide range of molecular sieving applications, for example, an everyday laboratory use as drying agent for organic solvents.[15] This ability to selectively adsorb molecules also allows zeolites to separate gaseous mixtures, for instance, gases containing CH_4 and CO_2 can be separated by common zeolites such as NaX and CaA.[16] The removal of CO_2 from the CO_2/CH_4 gas is an important process for industries in upgrading the gas because the presence of CO_2 can reduce the heating value and leads to pipeline corrosion in the presence of water.[16, 17]

Water pollution by various organic materials has been a serious environmental problem. Adsorption is one effective technology for wastewater treatment. Zeolites with higher surface area can be used as adsorbent for the removal of organic material from water. For example, MCM-22 can be used to adsorb alcohols from water solutions; enhanced adsorption was obtained for alcohols with longer alkyl chains.[18] This material is also an effective adsorbent for a basic dye, methylene blue, removed from wastewater.[19] Zeolite Y is an efficient adsorbent in the removal of antibiotic contaminants; erythromycin (ERY), carbamazepine (CBZ) and levofloxacin (FLX) in wastewater remediation.[20]

The production of O_2 and N_2 from air using synthetic zeolites and pressure swing adsorption (PSA) cycles are increasingly important in industrial air separation. In air separation, CaA and NaX zeolites are mainly used as adsorbents. Since the N_2 molecule has larger quadrupole moment than O_2, it interacts more strongly with extra-framework cations in the zeolites, giving rise to localisation of N_2 molecules near accessible cations in contrast to a more diffused O_2 distribution. This indicates that cations in the zeolite play a crucial role in the N_2/O_2 selectivity.[21] On the other hand, Li^+ ion-exchanged X and A zeolites also have higher N_2/O_2 selectivity as well as higher N_2 capacities.[22] This is because of the smaller ionic radius of Li^+ possesses higher charge density and hence higher polarizing power. PSA using LiX zeolites is a highly efficient technology for air separation and is being used in industry.[21]

1.2.3: Catalysis applications

Zeolites are extremely useful as solid acid catalysts (e.g., ZSM-5, FER)[23] in many refinery processes including crude oil cracking, isomerisation and hydrocarbon synthesis. Cracking is responsible for the production of gasoline from low-value heavier fractions and isomerization is important for production of *iso*-alkanes or removal of undesired normal or slightly branched alkanes in fuels (e.g., diesel), increasing the octane number.[24, 25]

On the other hand, zeolites also serve as oxidation or reduction catalysts, often after metals have been introduced into the framework, for instances, titanium ZSM-5 zeolite is used in the production of caprolactam[26] and copper containing zeolites are used in the removal of NO from auto-exhaust streams.[27-33]

1.3: NO storage and releasing-materials

A number of materials have been proposed as delivery of exogenous nitric oxide (NO) where it may important for medical therapies. Using nitric oxide as a therapy would enable wound-healing times on chronic wounds (such as diabetic ulcers) to be reduced by several days.[34] It also could be used to coat medical instruments to prevent clotting after invasive surgery.[35] A common method of achieving such delivery method is store the gas inside the storage materials such as zeolites, Metal Organic Frameworks (MOFs), polymer etc. Nitric oxide will be discussed in much detail in section 1.12.

1.3.1: NO storage and releasing - zeolites

The negative charged framework of zeolites is compensated by cations such as Na^+, Ca^{2+}, Cu^{2+}, Co^{2+} and etc . The presence of extra-framework cations in the zeolite can interact with guests and sometimes help to convert the guest into an intermediate or final product.

Interactions of NO with transition metal ion exchanged zeolites are well known in catalytic and separation studies. Most researches studies focus on the destruction of NO, particularly in relation to selective catalytic reduction (SCR) deNOx process, removal of nitrogen oxides (NOx) from exhaust gases or other lean-burn engines. This is important to control global air pollution. Within zeolite families, Cu-ZSM-5 is the most famous catalyst to catalyse NO decomposition. [28, 36, 37]

Recently, zeolites have been proposed to use in NO storage and delivery which is important in medical therapies. NO storage and delivery using zeolites are related to the pressure swing adsorption (PSA) process. PSA have highlighted two types of adsorbed NO, reversible and irreversible.[33, 38, 39] Reversible adsorbed means NO weakly held which is predominantly physisorbed species. Irreversible adsorbed NO is relatively strongly held and it is not spontaneously released from the zeolite even at very low pressure. Irreversible NO is primarily chemisorbed with NO bound with the extra-framework cation residing in the zeolite channel through the nitrogen atom to form either mononitrosyl or dinitrosyl complexes.[40, 41] For example this can be described with Cobalt-NO complex structure in the Co-LTA zeolite[40] shown in Figure 1.4. Irreversible adsorption is a good method for storing gas in the material since it not easily released. The irreversible NO can be released when the zeolites are exposed to the moisture since zeolites have higher affinity to water; water molecules displace the NO bound with cation in the zeolite.[42] NO stored in zeolites also can be released by heating sample to a high temperature. However, this method is biological unfriendly. Recently, Morris and co-workers began storing and releasing NO using zeolites. They found that zeolite-A displays good adsorption NO capacity depending on the extra-framework cations in the zeolites and the amount of exchanged metal present. They also demonstrated the anti-thrombus studies proving that the NO-containing zeolite prevents aggregation of platelets.[41-44] A subsequent publication has shown that trials on human skin were successful and the NO-releasing zeolite causes no harm to the skin while an acidified cream (a competing NO-releasing therapy) actually causes quite severe damage to the skin.[45]

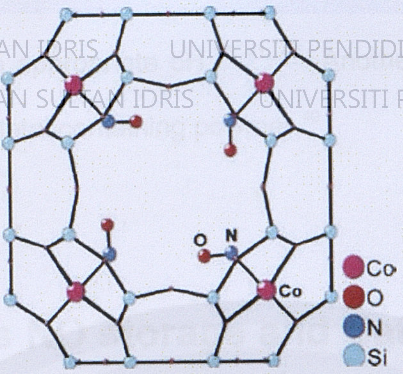

Figure 1.4: Structure of Cobalt-NO complex in Co-LTA zeolites. The cobalt is bound to three oxygen atoms of a six-ring unit in the zeolite framework and bond to the nitrogen of a bent mononitrosyl ligand.[40, 41]

1.3.2: NO storage and releasing - MOF

Metal organic frameworks (MOFs) also have a great potential in gases storage due to their high surface area. HKUST1 shows a higher uptake of NO compared with the zeolites but the amount NO release from HKUST-1 is a smaller than the amount actually adsorbed. However, NO-loaded HKUST-1 is still completely inhibits platelet aggregation even though only a small amount of NO has been released.[46] Ni-CPO-27 and Co-CPO-27 have a greater uptake of NO at room temperature with a perfect release upon exposure to the moisture. The adsorption-storage-delivery cycle of the significant amount of NO using M-CPO-27 (M= Ni, Co) shows that it to be active in the vasodilation of porcine arteries.[47]

1.3.3: NO delivery using polymer

Another method to deliver exogenous NO is based on polymer or silica functionalized with secondary amines that reacts with NO to form ionic diazeniumdiolates. Two NO molecules react with each amine (giving rise to trivial name NONOate) and are released from the particle on contact with moisture at an appropriate pH.[35, 41, 48] Another method also explored is light-activated release of NO from metal containing polymer.[49]

1.3.4: Simultaneous NO storage and Catalytic NO production using zeolites

Zeolites and MOFs are good for NO storage and delivery agent, however one of the drawbacks of this approach is the reservoir stored NO gas in the materials is finite and cannot be replaced easily especially for longer-term implant. Therefore, an alternative way to deliver the active gas is to produce the gas chemically using catalytic method from suitable substrate. Morris *et.al* have reported that copper containing zeolites such as Cu-X , Cu-ZSM-5 [50] and Cu-MCM-41[51], are not only good for NO storage and delivery, but they also produce the gas by catalytic reaction where the active Cu(I) species in zeolites transform NO_2^- (substrate) to NO.[50, 51] Thus, combining these two methods (gas storage and catalytic gas production) has potential to significantly increase the lifetime of a gas delivery material beyond what is possible with gas storage alone.

1.4: Zeotype

Zeotype molecular sieves are a family of solids displaying identical structure to zeolites but different elements composition present in them. [2] For instance, aluminophosphate ($AlPO_4$), titanosilicate (ETS), gallium phosphate (GaPO), silicoaluminophosphate (SAPO), germanosilicate (ITQ-37), metal aluminophosphate (MAPO) and etc. Most zeotypes are found as synthetic zeotype and they are extensively used in catalysis and absorbent for the molecular separation.[52]

1.4.1: Aluminophosphates

In early 1980, Wilson and co-workers reported that aluminophosphate ($AlPO_4$- n) where n refer to discrete structure type;[53] represent the first family of zeotype framework oxide synthesized in the absence of silicon.[54] There are three examples of $AlPO_4$-n analogous to natural zeolite topologies; AlPO-24 (analcime type), AlPO-20 (sodalite type) and AlPO-17 (enrionite/offretite type).[54] The main dissimilarity between AlPO-n and zeolites are fully tetrahedral AlPO-n always have neutral frameworks in contrast to negatively charge of zeolite. Secondly, aluminium atom in AlPO-n can exist in four, five or six coordinated in framework instead of zeolite where the aluminium is always in tetrahedral coordination.[55]

The open frameworks AlPO-n can be categorized into two classes, they are neutral frameworks AlPO-n with Al/P=1 and anionic frameworks AlPO-n with Al/P ≤ 1. Neutral frameworks $AlPO_4$-n are strictly generated by alternating AlO_4^- and PO_4^+ tetrahedra.[53] As in aluminosilicate zeolites, AlPO-n frameworks are built up from Al-O-P bonds following Löwenstein's rule where Al–O–Al bonds are avoided.[53, 56] The P–O–P bonds are not to be stable in these structures. Thus by avoiding of Al–O–Al and P–O–P bonds, open-frameworks of AlPO-n with even-numbered rings can be formed.[53] The general molecular formula of these materials can be written as **$[(AlO_2)_x(PO_2)_x].YH_2O$**.[55] Anionic frameworks AlPO-n molecular sieves are made up from combination of Al-centered polyhedra (AlO_4, AlO_5, AlO_6) and P-centered tetrahedral **$[P(O_b)_n(O_t)_{4-n}]$** where **b** denoted a bridging **O**, **t** is a terminal **O** and **n** is an integer. The presence of terminal P-OH and/or P=O groups or $Al(PO)_n$ (n=5,6) in the anionic frameworks AlPO-n has changed the Al/P ratio from the unity of AlPO-n frameworks. The negative charges of anionic framework

AlPOs are normally compensated by protonated organic templates to stabilise the framework. In addition the protonated templates also interact with P-OH and/or P=O groups through H-bonding to stabilise the framework. A notable example of this kind material is JDF-20 with Al/P = 5/6.[53] The anionic frameworks AlPO-n also have various low-dimensional framework structures such as 2D layers with various porous sheets and sheet stacking sequences and 1D chains which might act as fundamental building blocks for complex structures. Generally, the anionic AlPOs are unstable upon removal of the occluded protonated templates by calcination.

1.4.2: Silicoaluminophosphates (SAPOs) and Metal aluminophosphates (MAPOs)

Although the three dimensional (3D) AlPO-n materials possess excellent stability at 400 to 600 °C,[54] these kind of molecular sieves cannot be used in catalysis directly. This is because they are lacking acid sites due to the neutral framework. Nevertheless, this deficiency can be improved by isomorphous substitution of Al and P atoms in AlPO-n frameworks with other heteroatoms such as Si^{4+}, Mg^{2+}, Co^{2+}, Mn^{2+}, Zn^{2+}, $Fe^{2+}$and etc. to produce **silicoaluminophosphates (SAPOs)** or **metal aluminophosphates (MAPOs).** For examples SAPO-34[57], SAPO-5[58], MgAPO-20[59], MnAPO-11[60], FAPO-5[61], ZnAPO-LAU[62] and so on. To date about 24 unique pure MAPO zeotype structures belong to AlPO-n analogous have been reported as shown in Table 1.1.[63]

Table 1.1: Structure and composition features of MAPO molecular sieves (D=dimension and R= ring)[63]

Type Material	Framework type	Metal heteroatom	Channel system	AlPO$_4$-n analogue
ACP-1	ACO	Co, Fe	3D, 8R	-
AlPO-18	AEI	Co, Mn, Zn, Fe, V, Mg, As, Ga, Ge,Ti, Ni	3D, 8R	+
AlPO-11	AEL	Co, Mn, Ge, Mg, Nb, Ti, V, Fe, Cu, Ni,Zn, As, Be, Cr, Cd	1D, 10R	+
AlPO-EN3	AEN	Co, Mn, Cu	2D, 8R	+
AlPO-5	AFI	Co, Zn, Mn, Fe, Mg, Cr, Ni, V, Cu, Mo. Sn, Ti, Zr, Ca, Sr, Ba, Be, Ge, Li, Ce, Cd	1D, 12R	+
AlPO-14	AFN	Mn, Mg, Zn, Cr, Co	3D, 8R	+
AlPO-41	AFO	Co, Mn, V, Zr, Ti	1D, 10R	+
AlPO-40	AFR	Co, Zn	2D, 12R x 8R	+
MAPO-46	AFS	Co, Mg, Mn, Ni, Zn	3D, 12R x 8R x 8R	-
SAPO-56	AFX	Mg	3D, 8R	-
CoAPO-50	AFY	Co, Zn, Mg, Mn	3D, 12R x 8R x 8R	-
Analcime	ANA	Co	3D, 8R	+
AlPO-C	APC	Co	2D, 8R	+
AlPO-16	AST	Co, Mn, V, Cr	0D, 6R	+
MAPO-39	ATN	Zn, Mg, Co	1D, 8R	+
AlPO-31	ATO	Co, Mn, Zn, Mg, Cr, Cu, Cd, Ti, V	1D, 12R	+
MAPO-36	ATS	Co, Zn, Mg, Fe, Ti, V, Mn, Be, Ga	1D, 12R	+
AlPO-25	ATV	Co	1D, 8R	+
AlPO-21	AWO	Co, Ni, Fe, Cr	1D, 8R	+
Beryllophosphate-H	BPH	Mg	3D, 12R x 8R x 8R	-
Chabazite	CHA	Co, Zn, Mn,Mg, Fe, Ni, Cu, Cr, Be, Li	3D, 8R	+
DAF-1	DFO	Co, Mg, Ni	3D, 12R x 10R x 8R	-
DAF-2	DFT	Co	3D, 8R	-
Edingtonite	EDI	Co, Cu	3D, 8R	-
Eironite	ERI	Co, Fe, Mg, V	3D, 8R	+
Faujasite	FAU	Co, Cu, Zn	3D, 12R	-
Gismondine	GIS	Co, Mg, Zn, Mn	3D, 8R	+
CoAPO-CJ40	JRY	Co, Zn, Mn, Fe	1D, 10R	-
Laumontite	LAU	Co, Zn, Mn, Fe	1D, 10R	-
Levyne	LEV	Co, Zn, Mg	2D, 8R	+
Linde type A	LTA	Co, Zn, Mg, Mn, Fe	3D, 8R	+
Merlinoite	MER	Co	3D, 8R	-
UiO-28	OWE	Co, Mg	2D, 8R	-
Phillipsite	PHI	Co, Zn	3D, 8R	-

Incorporation of divalent or tetravalent heteroatoms with AlPO-n frameworks would generate negative charge thereby creating a potential solid acid catalyst. Normally the negative charged is balanced by H^+ ion to form strong Bronsted acid site groups.[64, 65] The metal ion could act as Lewis acid sites when interacting with Bronsted entities as shown in Figure 1.5.[65]

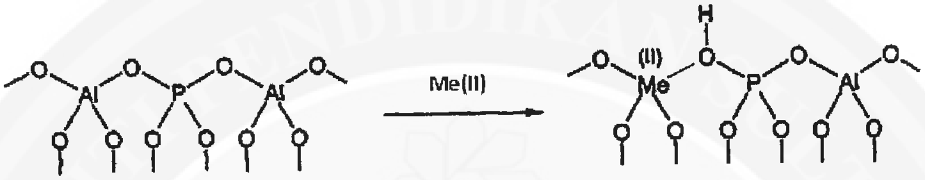

Figure 1.5: Model explaining the way isomorphous substitution of divalent metal generates surface acidity. A surface Bronsted-Lewis interaction is apparent.[66]

There are three types of isomorphous substitution mechanism (SM) of Al and P occurring in AlPO-n which are illustrated in Figure 1.6. First the substitution mechanism 1 (SM I) involves the aluminium substituted with valence atoms +1, +2 and +3 resulting the M-O-P bond. The second substitution mechanism 2 (SM II) is for phosphorus replaced by valence elements +4 or +5 to form M-O-Al bond. The third substitution mechanism 3 (SM III) is substitution of pairs of adjacent Al and P atoms. Only Si exhibitsSM III.[67] Other kinds of the substitutions are not mentioned in Figure 1.6, as they are very unlikely because they would generate either too negative a charge density or high positive charge. Figure 1.6 shows that the negatively charged frameworks generated from the isomorphous substitution also can be balanced by positively extraframework species such as quaternary ammonium cation, protonated amines, hydroxonium ion or transition metal ions.[68] In addition incorporation of transition metal into $AlPO_4$-n framework would produce the isolated redox centre to the material.[69]