CHAPTER 1

INTRODUCTION

1.1 GENERAL ASPECTS OF ALUMINOPHOSPHATES

Conventionally, a zeolite is a crystalline aluminosilicate or silicate polymorph based on corner-sharing \( \text{TO}_4 \) (\( T = \text{Si and Al} \)) tetrahedral forming a three-dimensional four-connected framework with uniformly sized pores of molecular dimensions (Breck 1974). Zeolite materials are very important in industrial technologies such as catalysis, sorption and ion-exchange. At the onset of 1980s, a novel class of crystalline, microporous aluminophosphates (AlPOs) was reported by Wilson et al (1982 and 1982a) at Union Carbide, representing the first family of framework oxide molecular sieves synthesized without silica. This discovery opened the door to a new era in open-framework inorganic materials (Cheetham et al 1999). The aluminophosphate molecular sieves known as AlPO\(_n\)-n (n refers to a distinct structure type) were prepared with a wide range of pore sizes by hydrothermal synthetic technique in the presence of organic amines or quaternary ammonium cations as templates or structure directing agents (SDA) (Pastore et al 2005 and Wilson 1991 and 2001). The structures of AlPO\(_n\)-n are based on strict alternation of \( \text{AlO}_4 \) and \( \text{PO}_4 \) tetrahedra forming a neutral open-framework. The lattice Al and/or P atoms can be partially replaced by silicon and/or other elements to form frameworks with Brønsted, Lewis acid sites and/or redox metal centers (Flanigen et al 1988 and Hartmann and Kevan 1999).
Their general formula can be expressed as

\[ [(\text{AlO}_2)_x(\text{PO}_2)_y] \cdot y\text{H}_2\text{O} \]

indicating that, unlike most zeolites, aluminophosphate molecular sieves are ordered with Al/P ratio that is always unity. However, in spite of this, aluminophosphate molecular sieves exhibit enhanced structural diversity.

The discovery of open framework AlPOs has brought some conceptual breakthrough for traditional microporous compounds, e.g., the framework elements not only limited to Al and Si atoms; the upper limit of pore size not only delimited to 12-ring; the primary building units not only defined to tetrahedral. Particularly the on going search for new structures provides some mechanistic clues on the formation of open framework materials. Ultimately, the crystallization mechanism of microporous materials must be understood in order to rationalize the synthesized materials with desired structures, compositions and properties. The discovery of AlPOs also improved the current application areas of microporous materials (Thomas et al 1999 and Thomas 1999). One of the important promising areas of application of AlPOs is in catalysis where aerial oxidations are possible using linear and cyclic hydrocarbons (Thomas et al 2001). The nanosized channels of AlPO$_n$-$n$ also present suitable host systems for the fabrication of advanced functional materials, e.g. monosized single walled carbon nanotubes (Wang et al 2000).

1.2 EXISTENCE OF ALUMINOPHOSPHATES

The interaction between aluminium and phosphorus oxides to form stable structures occurs to a considerable extent in nature. The nine naturally occurring neutral aluminophosphate minerals are berlinite (AlPO$_4$), variscite and metavariscite (AlPO$_4$.2H$_2$O), augelite (Al$_2$PO(OH)$_3$), senegalite
(Al$_2$(OH)$_3$(H$_2$O)(PO$_4$)), wavellite (Al$_3$(OH)$_3$(PO$_4$)2H$_2$O), trolleite (Al$_4$(PO$_4$)$_3$(OH)$_3$), bolivarite (Al$_3$(PO$_4$)(OH)):4-5H$_2$O) and evansite (Al$_3$PO$_4$(OH)$_6$ 6H$_2$O). To date, at least 200 structure-types of open framework AlPO$_4$-n molecular sieves, their isomorphous substitute analogues and anionic AlPO$_4$ framework.

1.3 STRUCTURAL ASPECTS OF ALUMINOPHOSPHATES

1.3.1 Classification

The open framework AlPO$_4$-n reported to date comprise a wide range of structures and compositions. In terms of electrostatic properties and Al/P ratios of the frameworks, they can be classified into two major categories viz., (i) neutral framework AlPO$_4$-n with Al/P = 1 and (ii) anionic framework AlPO$_4$-n with Al/P ≤ 1.

1.3.1.1 Neutral framework

The characters of AlPO$_4$-n include a neutral framework and a univariant framework composition with Al/P = 1 (Bennett et al 1986). Subsequent efforts to incorporate other elements have led to the formation of AlPO$_4$-based molecular sieves such as SAPO (S: Si), ELAPO (El: Li, Be, B, Ga, Ge, As, Ti, etc.), ELAPSO, MeAPO (Me: metal) and MeAPSO. Even though some of them have not been found pure AlPO$_4$-n counterpart yet, these structures can be ideally described using a hypothetical AlPO$_4$-n lattice with alternate Al and P sites as the basis. To date, 167 zeolite framework type codes have been identified (Baerlocher et al 2001). The AlPO$_4$-based molecular sieves include 51 unique structure types with extra-large pores (>12-ring), large pores (12-ring), intermediate pores (10-ring), small pores (8-ring) and very small pores (6-ring). These structures include 16 zeolite analogues such as chabazite (AlPO$_4$-n = 34, 44 and 47), erionite (AlPO$_4$-17),
faujasite (AlPO₄-37), gismondine (AlPO₄-43), levynite (AlPO₄-35), linde type A (AlPO₄-42), sodalite (AlPO₄-20) and 35 novel structures such as VFI (VPI-5), AEL (AlPO₄-11) and AFI (AlPO₄-5). Figure 1.1 illustrates several representative AlPO₄-n molecular sieves with different pore openings and dimensions including VFI (VFI): 18-ring (1.27 x 1.27 nm), AlPO₄-8 (AET): 14-ring (0.79 x 0.87 nm), AlPO₄-5 (AFI): 12-ring (0.73 x 0.73 nm), AlPO₄-11 (AEL): 10-ring (0.40 x 0.65 nm), AlPO₄-41 (AFO): 10-ring (0.43 x 0.70 nm) and AlPO₄-25 (ATV): 8-ring (0.30 x 0.49 nm). Apart from aluminosilicate or silica zeolites, AlPO₄-based molecular sieves constitute a major class of zeolitic materials. These AlPO₄-based materials are normally stable upon removal of the occluded template molecules and exhibit excellent thermal stability up to 1000 ºC. These materials are mildly hydrophilic. The major structures in the AlPO₄-n molecular sieves are listed in Table 1.1.

1.3.1.2 Anionic framework AlPOs

In contrast to neutral framework AlPO₄-n with Al/P = 1, most of the anionic framework AlPOs have Al/P ratio less than unity (Yu and Xu 2003). The structures of anionic AlPOs comprise three dimensional and low dimensional frameworks made up of alternate Al-centered polyhedra (AlO₄, AlO₅ and AlO₆) and P-centered tetrahedra P(O_b)ₙ(O_t)₄₋ₙ (b: bridging, t: terminal, n = 1,2,3 and 4) forming diverse stoichiometries. The existence of terminal P–OH and/or P = O groups or Al(OP)ₙ (n = 5 and 6) polyhedra results in the deviation of Al/P ratio from unity in the framework. Their Al/P ratios are found to 1/1, 1/2, 2/3, 3/4, 3/5, 4/5, 5/6, 11/12, 12/13, 13/18 and so on. Their frameworks exhibit fascinating structural architectures. A notable example is JDF-20 with Al/P = 5/6 (Huo et al 1992), which has the largest channel ring size of 20 among open framework AlPOs. Anionic framework AlPOs have also been prepared with diverse low dimensional
Figure 1.1  Representative AlPO$_4$-n molecular sieves with different pore openings
Table 1.1  Structures of AlPO₄-n molecular sieves

<table>
<thead>
<tr>
<th>n</th>
<th>IZA a structure code</th>
<th>Pore diameter/nm (ring)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>AFI</td>
<td>0.73 (12)</td>
</tr>
<tr>
<td>36</td>
<td>ATS</td>
<td>0.75 × 0.65 (12)</td>
</tr>
<tr>
<td>37</td>
<td>FAU</td>
<td>0.74 (12)</td>
</tr>
<tr>
<td>40</td>
<td>AFR</td>
<td>0.43 × 0.70 (10)</td>
</tr>
<tr>
<td>46</td>
<td>AFS</td>
<td>0.64 × 0.62 (12)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.4 (8)</td>
</tr>
<tr>
<td>11</td>
<td>AEL</td>
<td>0.63 × 0.39 (10)</td>
</tr>
<tr>
<td>31</td>
<td>ATO</td>
<td>0.54 (12)</td>
</tr>
<tr>
<td>41</td>
<td>AFO</td>
<td>0.43 × 0.70 (10)</td>
</tr>
<tr>
<td>17</td>
<td>ERI</td>
<td>0.36 × 0.51 (8)</td>
</tr>
<tr>
<td>18</td>
<td>AEI</td>
<td>0.38 (8)</td>
</tr>
<tr>
<td>33</td>
<td>ATT</td>
<td>0.42 × 0.46 (10)</td>
</tr>
<tr>
<td>34</td>
<td>CHA</td>
<td>0.38 (8)</td>
</tr>
<tr>
<td>35</td>
<td>LEV</td>
<td>0.36 × 0.48 (8)</td>
</tr>
<tr>
<td>39</td>
<td>ATN</td>
<td>0.4 (8)</td>
</tr>
<tr>
<td>42</td>
<td>LTA</td>
<td>0.41 (8)</td>
</tr>
<tr>
<td>43</td>
<td>GIS</td>
<td>0.31 × 0.45 (8)</td>
</tr>
<tr>
<td>44</td>
<td>CHA</td>
<td>0.31 (8)</td>
</tr>
<tr>
<td>47</td>
<td>CHA</td>
<td>0.38 (8)</td>
</tr>
<tr>
<td>16</td>
<td>AST</td>
<td>(6)</td>
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<tr>
<td>20</td>
<td>SOD</td>
<td>(6)</td>
</tr>
<tr>
<td>25</td>
<td>ATV</td>
<td>0.30 × 0.49 (8)</td>
</tr>
<tr>
<td>8</td>
<td>AET</td>
<td>0.79 × 0.87 (14)</td>
</tr>
<tr>
<td>VPI-5</td>
<td>VFI</td>
<td>1.21 (18)</td>
</tr>
</tbody>
</table>

aInternational Zeolite Association
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. It is noteworthy that within each compositional family a wide variety of structure types have been observed. For instance, the 2D frameworks with Al/P = 3/4 show diverse layered structures. Most of the anionic framework AlPOs possess interrupted open frameworks with terminal P–OH and/or P=O groups. They are unstable upon removal of the occluded protonated template molecules by calcination.

1.3.2 Bonding Patterns

As that of zeolites, open framework AlPOs made up of Al–O–P bonds obey Löwenstein (1954) rule with avoidance of Al–O–Al bonds (only one exceptional case was reported in a layered AlPO containing Al–O–Al linkages (Huang and Hwu 1999). The P–O–P bonds do not appear to be stable in these structures. Thus the avoidance of Al–O–Al and P–O–P bonds endows open-framework AlPOs featured by even-numbered rings. In interrupted anionic frameworks, a part of Al–O–P linkages are missed and terminal P–OH and/or P=O bonds are commonly observed that interact with protonated templating molecules through H-bonds (Yu and Xu 2003). By using first-principle quantum chemical techniques, Corà and Catlow (2001) characterized the bonding properties of crystalline AlPOs to compare them with isostructural silica-based zeolites. Their calculation results reveal that silica polymorphs and AlPOs differ in the nature of bonding. The silica polymorphs consist of covalently bonded SiO₄ units, while AlPOs are shown to be of molecular ionic character and comprised of discrete Al³⁺ and PO₄³⁻ ions. The ionicity of the AlPO frameworks might be responsible for the major contrast between the chemistry of AlPOs and that of aluminosilicates relative to the nature and concentration of dopants that can be introduced into the frameworks. In AlPOs, ionic substitutional dopants introduce minor
perturbations to the host electric structure and therefore more readily replace Al in AIPOs than Si in zeolites.

1.4 TOPOLOGICAL CHEMISTRY OF ALUMINOPHOSPHATES

1.4.1 Building Units

The complex structures of open-framework AlPOs can be understood on the basis of their construction from fundamental building units. Topologically, the neutral framework AlPO$_4$-n molecular sieves can be described as four-connected 3D frameworks since Al and P atoms occupy the 4-connected vertices of 3D net. Most of the anionic framework AlPOs can be described as interrupted frameworks because part of the Al-O-P linkages are missed. The four connected 3D frameworks, typically for zeolite frameworks, can be thought to be constructed of finite secondary building units (SBUs). 18 SBUs have been listed for zeolites in the fifth edition of the ATLAS among which 8 occur in four-connected 3D AlPO$_4$-n frameworks (Figure 1.2). These SBUs are formed by primary building units (PBUs) of AlO$_4$ and PO$_4$ tetrahedra (known as TO$_4$) by sharing a common oxygen atom in their corners. Different linkages of these tetrahedral units lead to various sheet topologies. Figure 1.3 shows eight distinct 2D sheet structures. These SBUs are arranged in a specific geometrical pattern to form a definite crystal structure and uniform pore size.

1.4.2 Al and P Coordinations and Stoichiometries

The structural and compositional richness of AIPOs are attributed to the diverse coordination of Al and P atoms. The majority of AlPO$_4$-n molecular sieves are based on a four-connected network of corner sharing tetrahedra, i.e., AlO$_{4b}$ and PO$_{4b}$ (b: bridging oxygen between Al and P). There are a number of AlPO$_4$-n with mixed-bonded frameworks containing five or
Figure 1.2 Secondary building units (SBUs) found in AIP\textsubscript{4}-n based framework
Figure 1.3  Eight distinct 2D sheet structures (The SBUs constructing these sheets are also shown)
six coordinated Al atoms with one or two extra framework oxygen species such as OH and H$_2$O (Chen et al 1999). For instance, both VPI-5 and AlPO$_4$-8 contain AlO$_{4b}$(H$_2$O)$_2$ units; AlPO$_4$-17, -18, -20, -21 and -31 contain AlO$_{4b}$(OH) units. By omitting the OH and H$_2$O species, these frameworks can be idealized as a four-connected framework. Combinations of alternate Al and P atoms give rise to various framework structures and Al and P stoichiometries. According to Löwenstein’s rule, the number of Al–O$_b$ bonds must be equal to the number of P–O$_b$ bonds in open framework AlPOs. Consequently, the correlation of coordination environment of Al and P can be described in the following equation (1.1) (Yu and Xu 2003).

$$\sum_i m_{\text{AlO}_b} \cdot i_{\text{AlO}_b} = \sum_j n_{\text{PO}_j} \cdot j_{\text{PO}_j} \quad \text{(1.1)}$$

where $i(j)$ is the number of bridging oxygen coordinated to Al(P), $m(n)$ is the number of AlO$_{ib}$ (PO$_{jb}$) coordination, $\sum m_{\text{AlO}_ib}/\sum n_{\text{PO}_jb} = \text{Al/P}$, $i = 3, 4, 5$ and 6 corresponding to AlO$_{3b}$, AlO$_{4b}$, AlO$_{5b}$ and AlO$_{6b}$ units respectively; $j = 1, 2, 3$ and 4 corresponding to PO$_4$ units with one, two, three and four bridging oxygen respectively. Based on this equation, the detailed Al and P coordination for a given stoichiometry can be enumerated.

1.5 TEMPLATING IN THE CONSTRUCTION OF ALUMINOPHOSPHATES

Open framework AlPOs are synthesized by hydrothermal or solvothermal crystallization of reactive aluminophosphate gels in the presence of an organic base as the templating agent (or structure-directing agent) as in the synthesis of high-silica zeolites. These template species occupy the pores and cages of the structures and play an important role in directing the formation of a specific structure.
1.5.1 Types of Templates

A large variety of organic templates can facilitate the synthesis of open-framework AlPOs. So far, over 100 species have been used successfully as templates, typically involving quaternary ammonium cations and various organic amines including primary, secondary, tertiary and cyclic amines, and alkanolamines. Some stable metal ligand complexes such as \( \text{Cp}_2\text{Co}^{2+} \) and \( \text{Co(en)}_3^{3+} \) have also been used in the synthesis of AlPO materials. Very recently, ionic liquids have been used as both solvent and template for the preparation of SIZ-n type AlPO materials (Cooper et al 2004 and Parnham et al 2006). The one template multiple structure and multiple template one structure phenomena are remarkable in open framework AlPOs. For example, di-n-propylamine (Pr$_2$NH) has been used in the synthesis of at least ten different AlPO structure types such as AlPO$_4$-11, -31, -39, -41, -43, -46, -47, -50, H3/MCM-1 and H1/VPI-5/MCM-9, exhibiting low structure specificity. On the other hand, some structures readily form from many different templates, e.g., AlPO$_4$-5 is much less template specific and can be synthesized with more than 25 different templates. Few examples are given in Table 1.2. Tetrapropylammonium hydroxide (TPAOH) is a typical template for the synthesis of AlPO$_4$-5, which is stacked in a tripod arrangement with the head of one TPA ion suspended between three feet of the next TPA ion with a hydroxyl group neatly suspended between them (Bennett et al 1986). As seen in Figure 1.4, although this tripod arrangement is such a good geometrical fit with the cylindrical wall, the TPAOH is not a template in the true sense because of the inconsistency of the three fold molecular symmetry and six fold channel symmetry.

A few AlPO structures exhibit high template specificity. For example, AlPO$_4$-20 can be crystallized only with tetramethylammonium hydroxide (TMAOH). The spherical TMAOH molecule with 0.62 nm
Table 1.2 Templates used for the preparation of specific structure type

<table>
<thead>
<tr>
<th>Structure type</th>
<th>Typical template(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlPO₄-5</td>
<td>tetrapropylammonium hydroxide, tripopylamine, triethylamine, etc.</td>
</tr>
<tr>
<td>AlPO₄-11</td>
<td>dipropylamine, diisopropylamine</td>
</tr>
<tr>
<td>AlPO₄-14</td>
<td>isopropylamine</td>
</tr>
<tr>
<td>AlPO₄-17</td>
<td>quinuclidine, piperidine</td>
</tr>
<tr>
<td>AlPO₄-18</td>
<td>tetraethylammonium hydroxide</td>
</tr>
<tr>
<td>AlPO₄-20</td>
<td>tetramethylammonium hydroxide</td>
</tr>
<tr>
<td>AlPO₄-31</td>
<td>dipropylamine</td>
</tr>
<tr>
<td>AlPO₄-34</td>
<td>tetraethylammonium hydroxide</td>
</tr>
<tr>
<td>AlPO₄-35</td>
<td>quinuclidine</td>
</tr>
<tr>
<td>AlPO₄-36</td>
<td>tripropylamine</td>
</tr>
<tr>
<td>AlPO₄-46</td>
<td>dipropylamine</td>
</tr>
<tr>
<td>AlPO₄-47</td>
<td>dipropylamine and diethylethanolamine</td>
</tr>
</tbody>
</table>
Figure 1.4 Cylindrical channel in AlPO₄-5 and the stacking of encapsulated tetrapropylammonium hydroxide species.
diameter fits neatly into the sodalite cage. In some AlPOs, a mixture of templates appears to cooperatively direct the formation of structures. For instance, SAPO-37 is prepared by a mixture of TPAOH and TMAOH. Structural characterization shows the presence of TMA in the sodalite cages and TPA in the supercages. In the synthesis of AlPO$_4$-52, both Pr$_3$N and TEAOH appear to be necessary but only TEAOH is occluded in the structure. As with organic amine, water can also play an important structure directing role. A notable example has been seen in VPI-5. Even though VPI-5 is preferentially prepared in the presence of organic amines, the organic species are not occluded into the extra large 18 ring pores. Instead, water molecules form an intriguing H-bonded triple helix inside the channel (McCusker et al 1991).

1.5.2 Role of Templating

Templating has been a frequently discussed phenomenon in the synthesis of zeolites and related open-framework materials (Davis and Lobo 1992 and Zones et al 1996). So far, the relationship between the templating agents and the structures, usually known as templating effect, is still not fully understood. The term templating has been frequently used in the context of synthesizing high silica zeolites. One definition about templating was described by Lok et al (1983) as ‘the phenomenon occurring during either the gelation or the nucleation process whereby the organic species organizes oxide tetrahedra into a particular geometric topology around itself and thus provides the initial building block for a particular structure type’. Gel chemistry is also essential for the formation of microporous aluminophosphates. With the addition of organic base, the gel chemistry of aluminophosphate is altered, and the templating becomes operative only in the gel with right gel chemistry. Therefore the dual role of the organic templates in the synthesis of open framework AlPOs is evident. It serves the
important role of modifying the gel chemistry, and it also has a structure
directing effect.

The organic template plays at least two additional roles in the
product, i.e., stabilizing voids and balancing the framework charge. By
packing the cages and channels the organic template can increase the overall
thermodynamic stability of the template/lattice composite, so that the
metastability of the lattice alone is less critical (Wilson 1991 and 2001). The
stabilizing and charge balancing role of organic templates is quite evident in
anionic framework AlPOs. After removing the occluded template molecules
by calcination, the anionic frameworks normally collapse. Furthermore, the
templates also determine the stacking sequences of 2D layers. The template
molecules interact with host inorganic network with certain regularity, and
their interaction can be well described based on the interaction between SBUs
and protonated amino groups. This allows the template molecules to be
located with a reasonable success.

Even though a true templating effect, i.e., hand in glove fit between
organic and inorganic lattice, is less pronounced in the synthesis of open
framework AlPOs, it seems that an encapsulated organic species in the void
space of the inorganic host can adopt configuration that conforms best with
the surrounding aluminophosphate framework. For example, AlPO₄-12, -21
and -EN3 were synthesized with encapsulated ethylenediamine. It is stabilized
into optical isomers of the gauche form by intramolecular bonding in
AlPO₄-12 and -21, while it occurs in AlPO₄-EN3 as trans configuration with
N–C–C–N extended along a straight eight-ring channel. The empirical
evidence is that for a template to be successful there must be a ‘good fit’
between the guest molecule and the host framework formed. The importance
of template molecules appears not only in its role of structure directing but
also orientating the distribution of Si in the frameworks. Vomscheid et al
(1994) demonstrated the role of template in directing Si distribution in the lattice of SAPO materials.

In metal-substituted AlPOs, the template molecules also influence the degree of metal ion substitution in the frameworks. Lewis et al (1996) studied the influence of organic templates on the structure and the concentration of framework metal ions in microporous AlPO catalysts. Their calculations demonstrate that the degree of metal ion substitution in the framework is controlled not only by the relative stability of the framework but also by the need to accommodate the structure directing and charge compensating template molecules. Templates with higher charge/size ratios will allow a greater control over the ratio of metal substitution or heteroatom incorporation in the framework.

### 1.6 ISOMORPHIC SUBSTITUTION

Apart from the structural similarity with zeolites, AlPO₄ molecular sieves exhibit structural diversity due to their neutral framework in contrast to the negatively charged aluminosilicate. Secondly the aluminium atoms in the aluminosilicate framework are always tetrahedrally coordinated as compared to the four, five or six coordinated aluminium atoms present in the AlPO₄ framework as mentioned earlier in this chapter. Moreover they also offer compositional diversity. The Al and/or P ions in the AlPO₄ frameworks can be replaced by another element with similar cation radius and coordination requirements. However, elements incorporated in the AlPO₄ frameworks should possess radius ratios with oxygen, and T-O distances consistent with the applied crystal chemical concept for tetrahedral coordination. Their successful incorporation may be due to the flexibility of the microporous aluminophosphate framework and to specific interactions with the organic template, coupled with the mildly acidic gel chemistry used in the synthesis (Flanigen et al 1986).
Thus, the incorporation of silicon in silicoaluminophosphate molecular sieves results, SAPO-$n$ (Lok et al 1984 and 1984a). The addition of metal cations (M) yields porous metaloaluminophosphate, MeAPO-$n$ (Messina et al 1985 and Wilson and Flanigen 1986) or metalosilicoaluminophosphates, MeAPSO-$n$ (Lok et al 1985, 1985a, 1985b and 1985c and Patton et al 1985). In the SAPO materials, silicon substitutes for phosphorus or for aluminum-phosphorus pair, whereas the M cations substitute almost exclusively for aluminum. The MeAPO and MeAPSO materials encompass the characteristics of both zeolites and aluminophosphates which results in their unique catalytic, ion-exchange and adsorbent properties.

Flanigen et al (1988) elucidated the bonding concepts in AlPO$_4$-based molecular sieves. The linkages such as Al–O–P, Si–O–Si, Si–O–Al, Me–O–P and Me–O–P–O–Me have been observed, whilst the linkages such as P–O–P, P–O–Si, Al–O–Al, Me–O–Al and Me–O–Me appear to be unlikely. Based on these patterns, they proposed rules for framework cation siting of metal (Me) and Si in AlPO frameworks: (i) Me incorporation into a hypothetical Al site, (ii) Si into a hypothetical P site and (iii) 2Si for Al + P. Martens and Jacobs (1994) further elaborated the types of isomorphic substitution according to various substitution mechanisms schematized in Figure 1.5. The isomorphic substitution mechanism (SM) can be classified as (i) SM I—substitution of Al atoms. SM Ia, SM Ib and SM Ic refer to monovalent, divalent and trivalent element substitution of Al atoms respectively, thus resulting in a M–O–P bond, (ii) SM II-substitution of P atoms. SM IIa and SM IIb refer to tetravalent and pentavalent element substitution respectively, thus resulting in a M–O–Al bond and (iii) SM III—substitution of pairs of adjacent Al and P atoms. Si is the only element exhibiting SM III. The avoidance of Si–O–P bonds precludes a homogeneous substitution of 2Si for Al + P (SM IIIho, Figure 1.6 a). A heterogeneous substitution mechanism (SM IIIhe, Figure 1.6 b) instead of
Figure 1.5 Isomorphic substitution mechanisms in AlPO$_4$ based frameworks
Figure 1.6  Two-dimensional representation of Si substitution in an AlPO$_4$ framework (a) homogeneous substitution and (b) heterogeneous substitution
SM IIIho was proposed by Martens and Jacobs (1994) to reflect the presence of SiO$_2$ patches with only Si–O–Si and Si–O–Al bonds. The presence of additional Al within the SiO$_2$ patch produces a zeolite region. In some cases, the incorporation of other elements into AlPO$_4$ lattice represents combination of substitution mechanisms (Martens and Jacobs 1994). The bonding concepts have remained valid for all stable and calcined structures describable as tetrahedral nets.

1.6.1 Metaloaluminophosphates (MeAPOs)

Initially, Flanigen et al (1986) reported the incorporation of 13 elements into AlPO$_4$-5, including transition metal ions like titanium, manganese, iron, cobalt and zinc. The incorporation of transition metal ions into framework sites of aluminophosphate and silicoaluminophosphate molecular sieves is also of particular interest for the design of novel catalysts. Paramagnetic metal species are often introduced into molecular sieves to generate a catalytically reactive species or site. Various pretreatment or activation procedures are typically used to generate reactive metal ion valence states which are often paramagnetic. Transition metal ions can be incorporated by three different methods viz., impregnation, ion-exchange and isomorphous substitution. In the latter method the transition metal ion salt is incorporated directly into the synthesis mixture. Since the comprehensive papers of Flanigan et al (1986 and 1988) on ‘Aluminophosphates and the periodic table’, many studies have been published, claiming the isomorphous substitution of transition metal ions into the framework of different structure types (Hartmann and Kevan 1999).

It has been claimed that a variety of metals and transition metals can be incorporated into the aluminophosphate structure (Figure 1.7), but actual incorporation into the tetrahedral framework is difficult to prove.
Figure 1.7 Partial periodic table with transition elements introduced into aluminophosphates and silicoaluminophosphates

### 1.7 REQUIREMENT FOR COMPLEMENTARY CHARACTERISATION TECHNIQUES

The substitution of Al by divalent metal ions could generate Brønsted acid sites (bridging OH groups) as well as Lewis acid sites (corresponding to anionic vacancies deriving from missing lattice oxygens) in the aluminophosphate lattice. So the incorporation of a transition metal cation, which can easily change its oxidation number, also creates redox active site. The coupling of acidic with redox properties opens up routes towards shape selective bi-functional catalysts and design of novel catalysts. Clearly, knowledge of the location and the local structure (metal ion environment) of the incorporated metal ions is necessary for optimization and control of the catalytic activity in these systems. The catalytic properties of microporous materials are largely determined by the composition and structure on the atomic scale. Therefore, catalyst characterization is a lively and highly relevant discipline in catalysis.

Different characterization techniques are used in order to gain an insight into the location of the transition metal ions in an aluminophosphate framework. Generally, data on the location of the cations are collected with
difficulty since the metal concentration is usually low. It is necessary to use more than one method if a reliable conclusion is to be reached. Characterization techniques such as diffuse reflectance UV-Vis spectroscopy (DRS), electron spin resonance (ESR), electron spin echo modulation (ESEM), Fourier transform infrared (FT-IR) and diffuse reflectance infrared Fourier transform (DRIFT) spectroscopies are commonly applied. Nuclear magnetic resonance spectroscopy (NMR), Mössbauer spectroscopy, X-ray absorption near-edge structure (XANES) and extended X-ray absorption spectroscopy for fine structure (EXAFS) are also employed occasionally. Therefore, suitable complementary characterization techniques are necessary to understand the surface chemistry of microporous AlPO₄ materials.

In the following paragraphs, the main literature results about the characterization of Co, V, Fe and Ti doped AlPOs are resumed. In particular, AlPO₄-5 (AFI) and AlPO₄-11 (AEL) structures have been considered.

1.8 FAMILY OF AlPO₄-5 AND AlPO₄-11

The large pore AlPO₄-5 molecular sieve is composed of 4-ring, 6-ring and 12-ring straight channels which are interconnected by 6-ring windows. The main channels of this structure type are nearly circular and have a diameter of 0.73 nm. In the medium pore AlPO-11 the main channels are formed from 10-rings with an elliptical shape of 0.63 x 0.39 nm. Structural representations of AlPO₄-5 and AlPO₄-11 with different pore openings are shown in Figure 1.8. Incorporation of transition metal ions exhibiting redox properties in AlPO₄-5 and AlPO₄-11 framework with a well defined system of pores and cavities offers an excellent opportunity for the preparation of novel oxidation catalysts. The transition metal incorporated AlPO₄-5 and AlPO₄-11 have been widely studied about the isomorphous substitution of metal ions and their redox behaviour.
Several indirect tools have been proposed to confirm the incorporation of transition metal ions (TMIs) into framework sites of AlPO₄-5, AlPO₄-11 and other AlPO₄ materials. The replacement of Al³⁺ or P⁵⁺ by TMIs leads to increase of unit cell volume of the crystal structure assuming that the symmetry remains constant.

![Structural representation of AlPO₄-5 and AlPO₄-11 with different pore openings](image)

Figure 1.8 Structural representation of AlPO₄-5 and AlPO₄-11 with different pore openings

Typically the radii of Al³⁺ or P⁵⁺ are smaller compared to the TMIs and the resulting expansion is directly accessible by powder X-ray diffraction (XRD) employing equation (1.2) (Weckhuysen et al 1999)

\[
\frac{4}{3} \left( \frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2} = \frac{4 \sin^2 \theta}{\lambda^2}
\]

(1.2)

where \(a\) and \(c\) represent the unit cell parameters of a hexagonal system, \(\theta\) the diffraction angle, \(\lambda\) the X-ray wavelength and \(h\), \(k\) and \(l\) are the Miller indices. However, such lattice expansions are not always observed and even lattice contractions are reported in the literature (Weckhuysen et al 1999). It is plausible that the incorporation of a small amount of heteroatoms is not
always sufficient to change the unit cell dimensions within the experimental error.

Initially, isomorphous substitution was solely verified by chemical analysis. It is expected that the molar ratio of \((n_{\text{TMI}} + n_{\text{Al}})/n_{\text{P}}\) (for a TMI replacing Al) or \((n_{\text{TMI}} + n_{\text{P}})/n_{\text{Al}}\) (for a TMI replacing P) is equal to one. Although obeyed in several systems, this method is not direct and can be inaccurate especially when extra framework TMIs are present or different substitution mechanisms occur simultaneously. Some evidence for isomorphous substitution is obtained from the analysis of the weight loss of the material due to template decomposition by thermogravimetric analysis. The negative charge introduced by replacement of \(\text{Al}^{3+}\) or \(\text{P}^{5+}\) by a lower TMI are typically balanced by the positively charged template. It is often observed that decomposition of the positively charged template occurs at a higher temperature than that of the neutral one. Therefore from the thermogravimetric curves the amount of charged template and hence the extent of isomorphous substitution is estimated.

Replacement of \(\text{Al}^{3+}\) or \(\text{P}^{5+}\) by metal ions \((\text{Me}^{n+})\) results in the formation of acid sites. The number of acid sites formed can be measured by temperature programmed desorption of bases such as ammonia, pyridine or isopropylamine. A major problem with this material is to distinguish between Lewis and Brønsted sites. The formation of acid sites is also frequently assessed by catalytic test reactions. NMR line broading and determination of the void space in the \(\text{AlPO}_4\) crystals are also used. However, most of these criteria are not able to distinguish between isomorphous substitution and/or the mere presence of transition metal ions. So many spectroscopic techniques are widely used to study the coordination environment of the transition metal ions. Among these, ESR, IR, UV-Vis and XAS spectroscopies are used in a large number of studies as tools for characterization of these species.
1.8.1 Characterization of CoAPOs

Cobalt substituted aluminophosphates are the most extensively investigated MeAPO-n systems. In comparison to other first row transition metals, which usually prefer octahedral coordination geometry, Co$^{2+}$ ions adopt rather easily tetrahedral stereochemistry with oxide ions as ligands. This can be explained by the fact that the ligand field stabilization energies of Co$^{2+}$ ions ($d^7$) disfavour tetrahedral coordination relative to the octahedral one to a lesser extent than in the case for most other $d^n$ configurations.

The synthesis of cobalt-containing aluminophosphates has been described in many papers (Ahn and Chon 1997, Batista et al 1992, Canesson and Tuel 1997, Duke et al 1994, Hill et al 1996 and Singh et al 1995) and the preparation of large CoAPO-5 crystals has been achieved (Girnus et al 1994 and Yokomori and Kawachi 1995). The isomorphous substitution of cobalt into AlPO$_4$-n and SAPO$_4$-n has been studied extensively with many different techniques and in numerous structures including -5, -11, -14, -18, -25, -34, -36, -41, -44, and -50 (Akolekar 1994, Bennett and Marcus 1988, Ernst et al 1989, Marchese et al 1994, Meusinger et al 1994, Montes et al 1990, Prakash et al 1997 and Zhang and Harris 1995). Most studies focused on the nature of inserted Co ions and their redox behaviour. In this paragraph the main results based on different characterisation techniques will be resumed.

In situ time resolved synchrotron powder XRD studies of the hydrothermal synthesis of CoAPO-5 have been reported (Norby and Hanson 1998). Most studies agree that Co$^{2+}$ is substituting at least partially for Al$^{3+}$ (Verberckmoes et al 1998). Owing to their acidic and redox properties, cobalt containing aluminophosphates have been employed in a large number of catalytic studies. Nevertheless, the nature, coordination and oxidation state are still under debate (Šponer et al 2000, Thomson et al 1999 and Weckhuysen et al 2000). ESR studies in cobalt containing aluminophosphates are relatively
rare since the electron spin relaxation is so rapid as to require temperatures below 30 K to allow observation of Co$^{2+}$. Initial studies by Iton et al (1989) in CoAPO-5, CoAPO-34 and CoAPSO-34 at 4.2 K showed ESR of Co$^{2+}$ with $g = 5.6$. Calcination of as-synthesized materials led to a significantly reduced intensity of the Co$^{2+}$ ESR signal intensity. This reduced intensity (~23%) was ascribed to oxidation of Co$^{2+}$ to Co$^{3+}$ during the calcination procedure. Similar conclusions were drawn by Montes et al (1990) and others (Iton et al 1989, Kurshev et al 1994 and Xu et al 1990) who studied CoAPO-5.

A sharp signal ($g = 2.03$) was reported at room temperature by Montes et al (1990) in as-synthesized CoAPO-5, which was ascribed to Co$^{2+}$ being in a framework position. After ion-exchange of the sample with 0.1 N NH$_4$Cl and calcination, this sharp signal was not observed, but a very broad signal was seen at 77 K. This was explained by the authors as evidence for the oxidation of Co$^{2+}$ to Co$^{3+}$, but this interpretation is unclear. A similar signal ($g = 2.05$) was found by Prakash et al (1993) in their studies of CoAPO-5 using a different template for the synthesis. However, quantitative comparison of the experimental data on the amount of Co$^{2+}$ in as-synthesized, calcined and hydrogen or methanol treated CoAPO-5 samples indicate some disagreement between the results of different groups (Iton et al 1989, Kurshev et al 1994 and Xu et al 1990).

Temperature programmed desorption (TPD) and thermogravimetric analysis (TGA) of amine probe molecules showed that Co$^{2+}$ at low concentration is present in lattice positions and generates discrete Brønsted sites in a concentration equal to the cobalt content in both as-synthesized blue CoAPO-5 and calcined yellow-green CoAPO-5, consistent with no oxidation associated with the colour change (Xu et al 1990). On the basis of this finding, Kurshev et al (1994 and 1995) performed ESR experiments from 7 to 34 K. The experimental data in this temperature range show that the ESR
signal of Co\(^{2+}\) in calcined CoAPO-5 does not follow the Curie law and therefore that the ESR intensity of calcined samples is not directly associated with the amount of paramagnetic cobalt. At temperatures higher than 20 K no differences could be seen, which showed that the amount of Co\(^{2+}\) did not change upon calcination.

The temperature dependence of the ESR intensity follows the Curie law in as-synthesized CoAPO-5, but calcined CoAPO-5 exhibits an abnormal temperature behaviour, which is well explained by distortion of the tetrahedral symmetry of Co\(^{2+}\) to a lower dihedral symmetry by interaction of two oxygen molecules with cobalt. When the temperature decreases, the Co\(^{2+}\) ions tend to populate the Ms = \(\pm 3/2\) level, which is not ESR active, and the intensity of the observed ESR transition between Ms = +1/2 and Ms = −1/2 decreases. Therefore, changes of the local symmetry near the cobalt ion seem responsible for the intensity loss of the ESR signal rather than change in the oxidation state (Kurshev et al 1994 and 1995). These conclusions were also supported in two other independent studies (Berndt et al 1996 and Lohse et al 1995) using IR and UV-Vis spectroscopy.

Quantifying the number of Brønsted acid sites created by the bridging OH groups between Co\(^{2+}\) and a pentavalent phosphorus has also been utilised to investigate the redox properties of CoAPO materials based on the assumption that the number of bridging OH groups correspond to that of divalent cobalt species located in the framework. Following the intensity change of IR bands of adsorbed pyridine, Kraushaar-Czarnetzki et al (1991) concluded that the oxidation of CoAPO-5 and CoAPO-11 results in partial oxidation of the framework cobalt centres. In contrast Lohse et al (1995) noted that oxidation of framework Co\(^{2+}\) to Co\(^{3+}\) can not be confirmed on the basis of the concentration of bridging OH groups. Also by using IR
investigation, Naccache et al (1997) indicated that both calcined and reduced CoAPO-11 exhibited almost the same proton acidity.

The use of NMR spectroscopy in characterizing cobalt containing AlPO₄₅ has gained some momentum following the work of Canesson and Tuel (1997a) and van Breukelen et al (1997). The presence of cobalt in AlPO₄₅ typically results in signal broadening or appearance of multiple peaks. Montes et al (1990) observed that compared with AlPO₄₅-5, the NMR spectrum of CoAPO-5 contained multiple and intense side bands which indicates increased anisotropy. They ascribed this increase in anisotropy to strong dipolar coupling of phosphorus with paramagnetic Co²⁺ and, hence, as evidence for framework incorporation of Co²⁺ replacing aluminium. The observation of intense side bands is reported by several authors (Kraushaar-Czarnetzki et al 1991a, Prakash et al 1993 and 1996), while in other studies no such signals indicating increased anisotropy was reported (Prasad and Balakrishnan 1991 and van Breukelen et al 1997). However, measurements of impregnated Co/AlPO-5 and Co/AlPO-11 (Kraushaar-Czarnetzki et al 1991a and Peeters et al 1993) also showed NMR side bands consistent with increased anisotropy. Therefore, such increased anisotropy could not be used as evidence for isomorphous substitution of cobalt into aluminophosphates. Canesson and Tuel (1997a) showed for CoAPOs that a signal for P₁(3 Al, 1 Co) is found at about δ = 2500 ppm. They suggest that for every cobalt which is a direct neighbour to phosphorus, about 2500 ppm should be added to find a NMR signal for the phosphorus near cobalt. Application of the usual inversion recovery sequence distinguishes the relaxation processes of ³¹P nuclei between CoAPO-n and impregnated Co/AlPO-n molecular sieves (Chen et al 1992). The values of decay time for zero intensity for ³¹P NMR signals in an inversion recovery sequence are much reduced in CoAPO-5 in comparison to Co/AlPO-5. Mali and Raučić (1998) later showed that spin lattice relaxation rates are independent of the
nature of cobalt bonding and depends primarily on the effective cobalt concentration. Therefore, this method can only indicate whether or not paramagnetic centres are distributed uniformly throughout the sample.

The clustering of cobalt in CoAPO-5 has been studied by van Breukelen et al (1997) employing quantitative $^{31}$P NMR spectroscopy. They found that with increasing cobalt content in CoAPO-5 from 0.001 to 3.15 wt. %, the percentage of NMR visible cobalt decreases from 97 to 42 %. If the existence of extra framework cobalt can be ruled out, then around 10 NMR invisible phosphorus atoms per cobalt atom are needed to explain the observed decrease in signal intensity. The amount of NMR invisible phosphorus cannot be explained by assuming that only $^{31}$P signals of phosphorus in the first coordination sphere (four) become invisible. In contrast, if one assumes that the phosphorus atoms in the first and the third coordination sphere become invisible, then the amount of NMR invisible phosphorus per cobalt becomes 25, which is too high. A possible explanation for these observations is the formation of cobalt clusters of five or more cobalt atoms, which leads to about 10 NMR invisible phosphorus per cobalt atom. There are also few reports about preparation of other CoAPO materials and incorporation of high percentage (Co/Al (mole ratio) > 0.3) of Co$^{2+}$ in the framework positions (Feng et al 1997 and Rajić et al 2000).

While the isomorphous substitution of cobalt into several AlPO$_4$-n structures is commonly accepted, there is controversy about the redox properties of cobalt containing AlPO$_4$s involving Co$^{2+}$ and Co$^{3+}$ valence changes which is of considerable importance for redox reactions. The blue colour of as-synthesized materials is considered characteristic of tetrahedral Co$^{2+}$O$_4$ environment and is therefore consistent with cobalt occupying tetrahedral framework sites. Tetrahedral coordination of cobalt is also attributed to d-d electronic transitions in UV-Vis spectra (Verberckmoes et al
Calcination of the blue materials between 400 and 500 °C causes the colour to change to green, green-yellow or beige for high, medium and low cobalt contents respectively. It was suggested that these colour changes reflect varying degrees of oxidation to Co$^{3+}$ (Barrett et al 1996, Iton et al 1989, Prakash et al 1996, Schoonheydt et al 1989 and Shiralkar et al 1989), which might be dependent on the structure type (Sankar et al 1995). Barrett et al (1996) have used X-ray absorption spectroscopy to investigate different cobalt containing materials after synthesis, calcination and reduction. They found that while in as-synthesized materials Co$^{2+}$ is in a regular four coordinated site, the situation is more complex in calcined materials. In CoAPO-18 essentially complete oxidation of Co$^{2+}$ to Co$^{3+}$ is deduced with the local coordination of high spin Co$^{3+}$ being distorted. In contrast, incomplete oxidation was deduced for CoAPO-5 and CoAPO-36. Although precise mechanism of the oxidation is not clear, it is certain that oxidation of the framework Co$^{2+}$ to Co$^{3+}$ is vital for catalysis. A significant factor in facilitating the reaction is also the ability of Co$^{3+}$ to expand its coordination sphere. MgAPO-18 is totally inactive as an oxidative catalyst since the divalent ion cannot be raised to a higher oxidation state (Thomas et al 1999).

Chao et al (1992) investigated the redox behaviour of Co ions in CoAPO-5 using ESR and IR spectroscopy. They explained the spectroscopic results in terms of a species that they characterised as a dioxygen complex $O_2$-CoAPSO-5 in which the framework tetrahedral Co$^{3+}$O$_4$ increases its coordination and valence state by attaching a $O_2^+$ molecular ion to form the complex. Wu et al (1997) also proposed a dioxygen cobalt species in CoAPO-11 on the basis of their combined analysis of Raman and ESR spectroscopies. Calcination at 550 °C yields a diamagnetic hydroperoxo Co-O-O-H species which shows a Raman band at 1019 cm$^{-1}$. 
Diffuse reflectance UV-Vis spectroscopy has been frequently employed for the characterization of cobalt containing aluminophosphates (Kraushaar-Czarnetzki et al. 1991, Uytterhoeven and Schoonheydt 1994 and Verberckmoes et al. 1997). As-synthesized CoAPO-5 is usually characterized by a triplet at 16000, 17300 and 18500 cm⁻¹ which corresponds to 625, 578 and 541 nm (Kraushaar-Czarnetzki et al. 1991, Nakashiro and Ono 1993, Schoonheydt et al. 1989 and Uytterhoeven and Schoonheydt 1994). These absorptions are interpreted as due to Co²⁺ in a tetrahedral environment of oxygens in the AlPO₄ framework. After calcination the intensities of these bands are reduced and the band positions shift to 15500 cm⁻¹ (645 nm), 17300 cm⁻¹ (578 nm) and 19500 cm⁻¹ (513 nm). New intense bands also arise around 25200 cm⁻¹ (400 nm) and 31500 cm⁻¹ (317 nm). These bands are ascribed to Co²⁺ in a tetrahedrally distorted environment and to Co³⁺ respectively. This structural Co³⁺ is then reported to be reducible with hydrogen, carbon monoxide, NO, methanol, acetone, toluene and water (Berndt et al. 1996). Spectroscopic criteria for the distinction between framework and extra framework Co²⁺ in CoAPO-5 were proposed by Verberckmoes et al. (1997 and 1998). Tetrahedral Co²⁺ in the lattice after calcination was related to bands at 5500 and 15150 cm⁻¹, tetrahedral Co²⁺ in extra framework positions to bands at 5500 and 16850 cm⁻¹ and octahedral Co²⁺ in extra framework positions to bands at 8100 and 19550 cm⁻¹. Upon calcination (pseudo) tetrahedral Co³⁺ in the framework, (pseudo) octahedral Co²⁺ in extra framework sites and (pseudo) tetrahedral Co²⁺ in both framework and extra framework sites could be formed depending on the crystalline quality of the sample. Upon subsequent reduction framework Co³⁺ is transformed to tetrahedral Co²⁺ with formation of a bridged hydroxyl with a typical stretching frequency of 3530 cm⁻¹ (Lohse et al. 1995, Thomson et al. 1999 and Weckhuysen et al. 1999).
The mechanism of redox process is still under discussion and there is disagreement as to the existence of trivalent cobalt in the calcined materials. Instead, it has been suggested that the colour changes are the result of distortions of the symmetry of the original tetrahedral environment without oxidation of the divalent cobalt ions (Kurshev et al 1994, Montes et al 1990 and Šponer et al 2000). The redox properties of CoAPO-5 and CoAPO-44 have been investigated by Berndt et al (1996) by temperature programmed reduction, oxidation and desorption. Furthermore, the acidity of the samples after oxidation or reduction treatment was investigated by temperature programmed desorption of ammonia and FT-IR using pyridine as a probe molecule. Berndt et al (1996) found no evidence for a valence state change of a significant portion of the framework cobalt ions or adsorption of oxygen on such sites. The formation of framework Co$^{3+}$ from Co$^{2+}$ was also not supported by Lohse et al (1997) who conducted IR investigation of basic probe molecules (NH$_3$, pyridine and acetonitrile) adsorbed on CoAPO-5 and CoAPO-44.

The correlation between cobalt framework substitution and acidity has been investigated in a series of papers by Thomas and co-workers (Chen et al 1994, Marchese et al 1994 and 1996 and Thomas et al 1994) mainly aiming at solid acid catalysts for methanol conversion to light olefins. To overcome the difficulties in revealing the Brønsted acidity of CoAPO catalysts, Marchese et al (1996a) proposed the use of nitrogen as a molecular probe, which is considered to be advantageous because nitrogen is a weaker base and is unlikely to affect the catalytic centers. The bridged OH stretching mode is shifted 100 cm$^{-1}$ to lower energy by adsorbing N$_2$ at 77 K because of the formation of a weak H-bond. This shift is about 10-20 cm$^{-1}$ smaller than that of the OH in H-ZSM-5, which suggests a lower Brønsted acidity for CoAPO-18 compared to H-ZSM-5.
The local environment of cobalt atoms in as-synthesized, calcined and hydrogen reduced CoAPO-34 and CoAPSO-34 have been studied by X-ray absorption spectroscopy (Rajić et al 1999 and Moen et al 1997). Cobalt is shown to be sited as Co$^{2+}$ in the framework and calcination of CoAPSO-34 (4.4 wt. % Co) leads to two-thirds of the Co$^{2+}$ being oxidized to Co$^{3+}$. Reduction of the sample leads to materials containing only Co$^{2+}$. The XANES spectra and their derivatives show a single edge peak at 7718 eV for as-synthesized CoAPSO-34 which is assigned to Co$^{2+}$. After calcination an additional peak at 7722 eV appears which is assigned to Co$^{3+}$. After subsequent reduction the 7722 eV peak only partially disappears. These results are in accordance with CoAPO-34 (Rajić et al 1999). The change of local environment of Co in CoAPO-18 has been investigated by the combined use of EXAFS and XANES (Thomas et al 1994). Detailed EXAFS investigations showed that tetrahedral Co coordination is slightly disordered, which is due to one Co-O bond being substantially longer (0.204 nm). A possible explanation is the protonation of the respective oxygen (Thomas et al 1994). The Co K-edge XAS of CoAPO-11 showed that cobalt ions are mainly in an oxidation state of +2 during redox treatment and that cobalt might distort from the regular tetrahedral site of as-synthesized form and possess an oxygen vacancy during redox treatment (Chao et al 1999).

Photoacoustic spectroscopy was applied to obtain information on CoAPO-44 (Han and Chon 1994). The spectra showed the presence of tetrahedral framework cobalt ions and cobalt with lower symmetry. The lower symmetry cobalt is more concentrated in the inner part of the crystallite of as-synthesized CoAPO-44, while it is distributed rather uniformly in the calcined sample. The spectra of CoAPO-5 and CoAPO-11 have shown, in agreement with results by Schoonheydt et al (1989), that the amount of cobalt that can be incorporated is limited to about 0.5 mol % (Lee and Chon 1996).
IR accompanied with EPR studies of NO adsorption on dehydrated, calcined and reduced CoAPO-5 indicated that NO molecule could be bounded to framework cobalt ions (Chao et al 1992). The interaction of NO with Co\textsuperscript{2+}/Co\textsuperscript{3+} redox centres in CoAPO-5 and CoAPO-18 has been studied by FT-IR and UV-Vis spectroscopy at 298 K and 85 K (Gianotti et al 1999). Two different Co\textsuperscript{2+} sites were found in these materials. Co\textsuperscript{2+} sites located in the framework of [Co\textsuperscript{2+}(OH)P] adsorb NO to form dinitrosyl complexes, which are reactive and form Co\textsuperscript{3+} and N\textsubscript{2}O, while Co\textsuperscript{2+} ions in structural defect sites act as Lewis acid sites.

In the view of the confusion still existing about the presence (or absence) and the possible nature of the redox centres in CoAPOs, detailed spectroscopic studies have been undertaken for CoAPO-5, CoAPO-11, CoAPO-41 and CoAPO-46 employing ESR, UV-Vis and X-ray absorption spectroscopy (Šponer et al 2000, Thomas et al 1999 and Verberckmoes et al 1998). These three independent studies report that oxidation of isomorphously substituted framework Co\textsuperscript{2+} to Co\textsuperscript{3+} is not (or only to a small extent) observed. The observed changes in the ESR spectra and the EXAFS data are best explained by the model proposed by Barrett et al (1996). Charge compensation in the calcined materials is achieved through the formation of anion vacancies following the loss of protonated templates (one vacancy for every two Co ions). Such vacancy formation will distort the framework in the proximity of Co\textsuperscript{2+} causing the observed effects on the ESR line width and EXAFS. UV-Vis spectra also confirm the formation of oxygen vacancies in the close vicinity of cobalt sites. It can be assumed that such anion vacancies are also responsible for the acid sites reported by some authors and the formation of radical cations. The formation of oxygen adducts as reported by several authors was ruled out.
1.8.2 Characterization of VAPOs

$V_2O_5$ based catalysts have been widely used in industry for many catalytic processes, including oxidation reactions under mild conditions. There is a large interest in vanadium analogues of molecular sieves based on zeolites and AlPO$_4$s based on their potential to catalyze oxidation reactions exploiting the high surface area and shape selectivity of microporous materials. The incorporation of vanadium into silicalite (Rigutto and van Bekkum 1991) and AlPO$_4$-n (Flanigen et al 1988a) has been reported. Most studies on vanadium containing aluminophosphates molecular sieves were devoted to VAPO-5 and VAPO-11, which were found to be active catalysts for selective oxidation of alkanes and cycloalkanes by oxygen in the gas phase (Concepción et al 1996), for alkene epoxidation and for benzylic oxidation by hydrogen peroxide in liquid phase (Rigutto and van Bekkum 1993). However, successful incorporation of vanadium into the framework of aluminophosphates is not straightforward. Therefore, several spectroscopic techniques have been used to investigate vanadium species in AlPO$_4$s.

There are several reports on vanadium containing aluminophosphate molecular sieves using ESR spectroscopy for the detection of $V^{4+}$ in VAPSO- and VAPO-5, -11, -31, -37, -40, and -41 and VPI-5 (Chao et al 1997, Chaudhari et al 1996, Flanigen et al 1988, Jhung et al 1990, Kulkarni et al 1995, Montes et al 1990a, Rigutto and van Bekkum 1993, Song et al 1993, Venkatathri et al 1995 and Whittington and Anderson 1993). ESR of these samples shows well resolved hyperfine splittings corresponding to $V^{4+}$ cations strongly bonded to oxygen ions in the matrix. Whittington and Anderson (1993) and Montes et al (1990a) found two different $V^{4+}$ species with very similar g tensor parameters. One of these species is also found in $V_2O_5$ impregnated AlPO$_4$-5 in which a single line at $g = 1.988$ is detected. This line is also found in pure $V_2O_5$. Seven well resolved hyperfine lines in VAPO-5
were ascribed to isolated vanadyl like V$^{4+}$ (I = 7/2) species (Jhung et al 1990). After calcination of VAPO-5 in flowing oxygen at 500 °C the signal intensity decreased by 40-fold (Jhung et al 1990), which is ascribed to the oxidation of the vanadyl like species to V$^{5+}$. The signal intensity could be increased by hydrogen reduction or high temperature exposure to organic molecules such as toluene or p-xylene. The reported results mainly underline the redox properties of vanadium in aluminophosphates and do not discuss the ESR parameters in terms of demonstrating possible framework incorporation of V$^{4+}$.

ESR results by Lohse et al (1995a), Frunza et al (2000) and Weckhuysen et al (1995) found no unambiguous evidence for true incorporation of V$^{4+}$ into tetrahedrally coordinated framework positions in AlPO$_4$s with AEL, AFI, ATO and CHA topology. In as-synthesized samples two signals with similar g tensor parameters were ascribed by Frunza et al (2000) and Weckhuysen et al (1995) to isolated (pseudo) octahedral V$^{4+}$. Very similar g tensor parameters were ascribed by Lohse et al (1995a) to isolated immobile VO$_2^{+}$ species in square pyramidal symmetry. Upon calcination, V$^{4+}$ ions were oxidized to tetrahedral V$^{5+}$ which could only be partially reduced to V$^{4+}$. However, the ESR detectable vanadium content was below 20% of the total vanadium.

ESR measurements on VAPO-11 material have shown that vanadium species are mostly isolated and in pseudo-octahedral coordination. In the case of a higher vanadium loading, polymeric species were observed (Frunza et al 2000). The framework vanadium (isolated VO$_4$ tetrahedron) in VAPO-5 was found most active and selective than extra framework vanadium species for oxydehydrogenation of propane (Blasco et al 1995, Concepción et al 1993 and Okamato et al 2000). Haanepen and van Hooff (1997) observed
tetrahedral species at low vanadium contents in VAPO-5 as well as VAPO-11 and the presence of various vanadium species.

There are different views on whether vanadium substitutes for Al\(^{3+}\) (Rigutto and van Bekkum 1993) or P\(^{5+}\) (Chao et al 1997, Lohse et al 1995a, Montes et al 1990a, Prakash and Kevan 1999 and Weckhuysen et al 1995). Based on EPR and \(^{27}\)Al, \(^{31}\)P NMR results, Jhung et al (1990) and Montes et al (1990a) assumed that V\(^{4+}\) substitutes for P\(^{5+}\). Rigutto and van Bekkum (1993) found that the composition of VAPO-5 is consistent with vanadium substitution for aluminium rather than for phosphorus. The replacement of P\(^{5+}\) by vanadyl VO\(^{2+}\) ions would generate negative charges to be neutralised by either H\(^+\) (H\(_3\)O\(^+\)) or a positively charged template molecule. Very recently, this model has been supported by the combined use of ESR and ESEM spectroscopies, which suggested that vanadium is located in the sites closer to aluminium than to phosphorus (Prakash and Kevan 1999 and Prakash et al 2000). XAS studies also claimed the presence of isolated monomeric VO\(^{2+}\) units in VAPO-5 bonded to two framework oxygens that could be coordinated by three water molecules (or one hydroxyl group and two water molecules) in the calcined form (Chao et al 1999). Upon dehydration, the coordination symmetry was found to shift gradually from either square pyramidal or octahedral to tetrahedral. This model was further refined by density functional theory (DFT) calculations and compared to experimental XAS and Raman spectra (Cheng et al 2000 and 2000a).

At low concentration, incorporated vanadium in VAPO-5 was mainly found in the well dispersed and immobilised monomeric vanadyl species with a square pyramidal or distorted octahedral coordination. V\(^{4+}\) could be oxidised to V\(^{5+}\) as detected by EPR and \(^{51}\)V NMR (Jhung et al 1990, Montes et al 1990a, Naccache et al 1997, Prakash and Kevan 1999 and Rigutto and van Bekkum 1993) and up to 80% of the vanadium could be
reduced back to monomeric vanadyl species with EPR parameters nearly identical to those present in the as-synthesised form. The same behaviour was confirmed by vanadium K-edge XANES and EXAFS studies (Cheng et al 2000). The coordination and oxidation number of vanadium sites in VAPO-5 following redox treatments were investigated by XANES/EXAFS (Chao et al 1999) showing \( V^{4+}/V^{5+} \) cycles are reversible. VAPSO-11 material showed similar redox behaviour with V ions in a phosphate environment with square pyramidal or distorted octahedral structures (Singh et al 1995a). A cyclic voltammetry study of VAPO-5 showed that the as-synthesised and calcined samples contained loosely bound \( VO^{2+} \) species that could be extracted from the framework and also revealed two distinct reversible processes \( (V^{5+}/V^{4+}) \) (Bedioui et al 1997).

Zahedi-Niaki et al (2000) investigated the vanadium incorporation in VAPO-5 (Blasco et al 2000), -11, -17 and -31 by XPS, NMR and ESR techniques. The authors suggested that in calcined VAPOs, isolated tetrahedral \( V^{5+} \) is present in framework positions, substituting for phosphorus. Extra framework isolated and/or polymeric vanadium in square pyramidal coordination were also present. Fan et al (2006) investigation showed the probable occupation of \( P^{5+} \) sites by \( V^{4+} \) over bimetal \( AlPO_{4}-5 \) using ESR and MAS NMR techniques. Combined ESEM and ESR results over VAPO-5 concluded that vanadium ions incorporated into \( AlPO_{4}-5 \) occupies a framework phosphorus site probably as a localised defect. Three kinds of vanadium species were observed (Prakash and Kevan 1999).

DRS-UV-Vis spectra of reference compounds such as \( V_2O_5 \), \( NH_4VO_3 \), Mg supported vanadium were compared with VAPO-5 samples of different vanadium content (Weckhuysen et al 1995). A band around 270-290 nm was assigned to isolated tetrahedral \( V^{5+} \) sites, supporting the incorporation of vanadium into the framework. A broad band in the region
350-450 nm suggests that some polymeric vanadium species, probably V$_2$O$_5$ like, are present. AlPO$_4$-5 samples impregnated with vanadium showed only slightly different UV-Vis spectra. These spectra also give a peak at 290 nm suggesting a tetrahedral environment for V$^{5+}$ and around 410 nm, which is ascribed by Blasco et al (1995) to polymeric forms of vanadium. The presence of different vanadium species in VSiβ zeolite was evidenced by DRS-UV-Vis and photoluminescence spectroscopies, but only the latter was able to clearly distinguish three kinds of tetracoordinated vanadium (Dzwigaj et al 1998).

Solid-state $^{51}$V NMR studies on V-containing catalysts (Rigutto and van Bekkum 1993) have shown that it is possible to obtain information on the symmetry environment of $^{51}$V by comparison with model compounds. The wide line $^{51}$V NMR spectra are mainly formed by a broad signal with a maximum slightly upfield from 300 ppm (reference VOCl$_3$), which is characteristic of V$^{5+}$ in an octahedral or square pyramidal environment (Blasco et al 2000a). Besides, a second band at 550 ppm is often observed indicating the presence of tetrahedral V$^{5+}$. The presence of tetrahedrally coordinated metal cations is often taken as evidence for isomorphous substitution. However, the bonding to extra molecules to increase the oxidation state (as it is suggested from the results obtained for V$^{4+}$) is not unusual and, therefore, the spectroscopic evidence is not ambiguous for both types of V$^{5+}$ environment in the framework positions (Blasco et al 2000a). $^{51}$V MAS NMR spectra of calcined VAPSO-11 show a narrow chemical shift distribution with an isotropic shift at $\sigma_{\text{iso}} = 540$ ppm. The $^{51}$V MAS NMR pattern is consistent with previously published literature of predicted square pyramidal or distorted octahedral vanadyl (V) species in VAPO-5. Similar $^{51}$V MAS NMR spectra were reported for VAPO-11 (Singh et al 1995a).
Yu et al (2002) found different vanadium species in VAPO-5 and VAPSO-5 using UV-Raman spectra and NMR. The vanadium species in VAPO-5 were mainly polymerized vanadium oxides together with minor amount of V$_2$O$_5$ particles. The presence of silicon atoms was found to be beneficial for the formation of isolated framework vanadium species in VAPSO-5.

Low temperature CO adsorption on VAPO-5 has been studied by IR spectroscopy. Carbonyl species were not formed with $V^{5+}$ ions in oxidized VAPO-5. Reduction resulted in the formation of $V^{4+}$ and $V^{3+}$, forming stable CO complexes at 85 K (Concepción et al 1999). ESR data also indicated high concentration of $V^{4+}$ in samples reduced hydrogen at 673 K in Blasco et al (1995). Chemical analysis and FT-IR spectra revealed that $V^{4+}$ ions are replacing P$_{5+}$ in the AlPO$_4$ framework of VAPO-31 (Venkatathri 2006).

1.8.3 Characterization of FeAPOs

The open framework structure coupled with the magnetic properties of inserted metal ions has opened the way to a new class of porous materials, namely, the magnetic sieves (Riou-Cavellec et al 1999). For this reason open framework iron phosphates have attracted great attention in the last few years (Pillai and Sahle-Demessie 2004 and Rajić et al 2002 and 2004). Iron substituted AlPOs also show catalytic activity in the pinacol rearrangement reaction (Hsu and Cheng 1998). The question of whether iron can be incorporated into the framework of AlPO-5 was addressed using different techniques such as powder X-ray diffraction, DRS-UV-Vis, IR, solid-state NMR, ESR, XPS and Mössbauer techniques (Ojo et al 1989, Ristić et al 2003, Wenqin et al 1989 and Zenonos et al 2002). The amount of iron reported to be incorporated into FeAPO-5 is rather low and therefore changes in the XRD pattern cannot be observed. A computational study of the substitution of Al by Fe$^{3+}$ in AlPO$_4$-5 shows that the substitution is energetically unfavourable
(Gonzalez et al 1999). Although, Messina et al (1985a) in the first report on FeAPO-5 supposed (based on chemical analysis) that the substitution of $\text{Fe}^{3+}$ and/or $\text{Fe}^{2+}$ for both $\text{Al}^{3+}$ and $\text{P}^{5+}$ occurs, it is now thought that Fe exclusively substitutes for Al. In the as-synthesized material, the coexistence of $\text{Fe}^{3+}$ and/or $\text{Fe}^{2+}$ is often found regardless of the iron salt employed (Ojo et al 1989). It has also been found that FeAPO-5 is an exceptionally good catalyst for the selective oxidation of cyclohexane in air (Raja et al 1999). The catalytic activity is attributed to the redox ability of $\text{Fe}^{3+}$ as an integral part of AlPO$_4$ framework. CO hydrogenation over Fe/AlPO-5 impregnated in aqueous solution showed no activity, while Fe/AlPO-5 impregnated in organic media showed 6 and 23 % conversion depending on the type of organic solvent (Ma et al 1994).

Typical ESR spectra of as-synthesized FeAPO-5 show five distinct signals at $g = 2.0, 2.2 - 2.4, 4.3, 5.2$ and $8.4$ (Catana et al 1995). Signals at $g = 2.0, 4.3$ and $6.0$ were earlier reported by Park and Chon (1992). While the band at $g = 2.0$ has been attributed to octahedrally coordinated iron in extra framework oxides. The signal at $g = 4.3$ is typically assigned to $\text{Fe}^{3+}$ tetrahedrally coordinated to oxygen (Gonzalez et al 1999 and Zenonos et al 2002). Catana et al (1995) suggested that the $g = 2.0$ signal is due to $\text{Fe}^{3+}$ in a tetrahedral site and the $g = 4.3$ line is ascribed to $\text{Fe}^{3+}$ in a distorted tetrahedral (defect) site. The total intensity of these two lines increases linearly with iron concentration, when the saturation level is exceeded (Catana et al 1995). The ESR intensities increase linearly with $1/T$ (Curie-Weiss behavior) in the temperature range 120-350 K. Similar results were obtained for FeAPO-11 molecular sieve (Prasad et al 1994).

The co-existence of $\text{Fe}^{2+}$ and $\text{Fe}^{3+}$ in as-synthesized samples was unambiguously revealed by XPS. The binding energies of Fe2p$_{3/2}$ at 712.3 and 708.4 eV are assigned to framework $\text{Fe}^{3+}$ and $\text{Fe}^{2+}$ respectively, while the
presence of non-framework Fe$^{3+}$ was evidenced by the Fe2p$_{3/2}$ peak at 710.5 eV. Calcination resulted in the total oxidation of Fe$^{2+}$ to Fe$^{3+}$ and as a consequence, in the disappearance of Fe2p$_{3/2}$ peak at 708.4 eV (Li et al 1988 or Ma et al 1994). More detailed information can be obtained by Mössbauer spectroscopy.

Iron is an element exhibiting Mössbauer effect. Mössbauer spectra of iron substituted AlPO$_4$-5 fit a singlet and two doublets, showing that two types of Fe$^{3+}$ and one type of Fe$^{2+}$ are present. The singlet (isomer shift $\delta = 0.188$) is assigned to tetrahedral Fe$^{3+}$ in the framework, while one doublet ($\delta = 0.3$) is assigned to Fe$^{3+}$ in an amorphous phase (Das et al 1992). The second doublet ($\delta > 1$) is assigned by Das et al (1992) to divalent iron, which sums to 10-20 % in FeAPO-5. The amount of divalent iron in FeAPO-11 is very low. Cardile et al (1990) also found Fe$^{2+}$ and Fe$^{3+}$ in their FeAPO-5 samples. Considering that an Fe$^{3+}$ salt was added to the synthesis gel, some reduction of Fe$^{3+}$ took place during sample preparation. If an Fe$^{2+}$ salt was used as a starting material, a large amount of extra framework Fe$^{2+}$ was found along with Fe$^{3+}$ in the framework (Li et al 1988). The Mössbauer spectrum of iron impregnated AlPO$_4$-5 exhibited a symmetric doublet due to quadrupolar splitting and an isomer shift near 0.3 mm/s (Ma et al 1994), which is attributed to superparamagnetic Fe$^{3+}$.

Hoppe et al (1995) synthesized FeAPO-5 in the presence of methylene blue to obtain innovative materials with special optical properties. Fe$^{2+}$ ($\delta = 1.4$) as well as Fe$^{3+}$ ($\delta = 0.8$) was found in the Mössbauer spectra. The addition of methylene blue had no influence on the Fe$^{2+}$/Fe$^{3+}$ ratio when FeSO$_4$ was used for the synthesis. The use of Fe$^{3+}$ led to irreversible decomposition of the complex. Mössbauer spectra of as-synthesised FeAPO-5 obtained using either Fe$^{2+}$ or Fe$^{3+}$ as the source of iron showed the presence of both Fe$^{2+}$ and Fe$^{3+}$ ions (Ojo et al 1989).
Using microwave synthesis, Bruckner et al (1998) prepared FeAPO-5 samples containing up to 3 mol% Fe. Mössbauer spectroscopy revealed that during crystallisation in air more than half of the Fe$^{2+}$ ions were oxidised, while only slight reduction occurred in gels containing Fe$^{3+}$ ions. The authors concluded that in as-synthesized and hydrated samples all iron ions are octahedrally coordinated residing either in defect sites (ESR signal at $g = 4.3$) or in intact framework sites (ESR signal at $g = 2$). Octahedral geometry is realized by coordination of two ligands within the pores (Bruckner et al 1998).

$^{57}$Fe Mössbauer spectroscopic studies were carried out on ferrocene guest molecules in AlPO$_4$-5 and AlPO$_4$-8 at 300 and 20 K (Lund et al 1994). The room temperature spectrum showed complete orientational freedom including flipping between parallel and perpendicular orientations which is still rapid on the Mössbauer time scale, whereas the low temperature spectrum showed either fixed molecules or rotations which are slow on the Mössbauer time scale.

Among other methods used for the characterization of FeAPO materials photoacoustic spectroscopy gave information on the incorporation of iron into the framework of aluminophosphates (Park and Chon 1992). All calcined FeAPO-5 samples showed spectra with four well resolved bands at 380, 410, 435 and 480 nm. These bands were also found in as-synthesized Fe silicalite and were assigned to Fe$^{3+}$ tetrahedrally surrounded by oxygen (Iton et al 1983 and Lin et al 1989).

Spinacé et al (1997) reported the incorporation of Fe$^{3+}$ into the framework of SAPO-37 (FAU) replacing tetrahedrally coordinated aluminium. The UV-Vis diffuse reflectance spectrum of FAPSO-37 showed two bands at $\lambda = 215$ and 250 nm, which were assigned to charge transfer from oxygen to an isolated framework Fe$^{3+}$. A very weak band at 370 nm was
also observed, related to forbidden d-d transitions of Fe$^{3+}$ in tetrahedral coordination, thus confirming the incorporation of iron into the lattice. Two ESR signals at $g = 4.3$ and 2.0 were observed and assigned to framework incorporated Fe$^{3+}$ and hydrated Fe$^{3+}$ in a symmetric tetrahedral framework site (Spinacé et al 1997). The presence of Fe$^{2+}$ and Fe$^{3+}$ in tetrahedral Al framework sites has also been confirmed by XANES in EXAFS and by the combination of several techniques in the large pore FeAPO-5, -18 and -36 (Ristić et al 2003, Shiju et al 2006 and Zenonos et al 2002).

1.8.4 Characterization of TAPOs

Tetrahedral titanium (Ti$^{4+}$) has been incorporated into several zeolites. These titanium modified materials show remarkable catalytic activity in oxidation reactions using dilute aqueous hydrogen peroxide under mild conditions. The titanium incorporated silicalite-1 (TS-1) has been one of the most relevant industrial catalysts in the last two decades. The catalytic activity is related to the tetrahedrally coordinated titanium incorporated in the framework (Bordiga et al 1994, Deo et al 1993, Huybrechts et al 1992, Millini et al 1992 and van der Pol et al 1992). These facts stimulated interest to investigate the possibility of incorporation of titanium into other frameworks. Several new titanium containing molecular sieves have been synthesized including TS-2 (MEL) (Reddy et al 1990), Ti-ZSM-48 (Serrano et al 1992), Ti-$\beta$(BEA) (Camblor et al 1992), mesoporous molecular sieves such as Ti-MCM-41 (Zhang and Pinnavaia 1996), Ti-MCM-48 (Chang and Kevan 2002), Ti-SBA-15 (Luan et al 2000), microporous titanosilicates (ETS-4 and ETS-10) (Kuznicki et al 1992) and also titanium aluminophosphates such as TAPO-5 (AFI) (Ulagappan and Krishnasamy 1995), TAPO-11 (AEL) (Zahedi-Niaki et al 1997) and TAPO-36 (ATS) (Zahedi-Niaki et al 1997). These TAPO materials show promising applications in catalysis such as in oxidation and epoxidation of hydrocarbons and alcohols (Zahedi-Niaki et al
TAPO catalytic oxidation activity was shown to be associated with framework incorporated Ti atoms, excluding the presence of leached Ti species in the reaction solution (Zahedi-Niaki et al. 1998). TAPSO materials were also found active in the epoxidation of cyclohexene using either H$_2$O$_2$ or Bu'OOH. The presence of SiO$_2$ increased the hydrophobic character of these materials (Tuel 1995). TAPO-5 and TAPO-11 materials were found active in the hydroxylation of phenol (Ulagappan and Krishnasamy 1995). Lee et al. (2003) found TAPO-5 active in the conversion of cyclohexene to adipic acid.

The isomorphous substitution of titanium as Ti$^{4+}$ in pure AlPO$_n$ materials is expected to be more difficult than other heteroatoms (Ulagappan and Krishnasamy 1995). There are only few reports about the presence of titanium in framework positions of AlPO$_4$-5 and AlPO$_4$-11. The incorporation of Ti$^{4+}$ has been studied by various methods. UV-Vis spectra of titanium containing AlPO$_4$s such as TAPSO-5 showed a single band centered near 230 nm indicating the presence of tetrahedral Ti$^{4+}$. The absence of a shoulder around 300 nm also indicated that anatase like phase in the sample (the most common impurity in Ti-containing zeolites) (Zahedi-Niaki et al. 1996 and Tuel 1995) was not formed during crystallisation.

Zahedi-Niaki et al. (1999) confirmed the presence of Brønsted acid sites by pyridine chemisorption in TAPO-5 and TAPO-36 using FT-IR and proton MAS NMR. The presence of Brønsted acid sites confirmed the insertion of titanium in the aluminophosphate lattice and supported the isomorphous substitution of titanium for phosphorus in these solids. Prakash et al. (1997a) used combined electron spin resonance (ESR) and electron spin echo modulation spectroscopic (ESEM) techniques to study the isomorphous substitution of Ti in TAPO-5 material and evidenced the formation of Ti$^{3+}$ ions upon reduction. $\gamma$-Irradiation and CO reduction were both effective
in producing paramagnetic Ti\(^{3+}\) species in TAPO-5 while \(\gamma\)-irradiation also produced (electron) hole centers (the unpaired electron spin being localized in a lone pair \(p\) orbital) on oxygen called V centres (defects). V centres were formed by ejection of an electron from the \(p_z\) orbital of an oxygen atom upon \(\gamma\)-irradiation, the electron being trapped within the material. An ESR signal with a rhombic g tensor (\(g_1 = 1.965\), \(g_2 = 1.92\), and \(g_3 = 1.879\)) was assigned to trivalent titanium in a framework site. The \(\gamma\)-irradiation of TiO\(_2\)/SAPO-5 gave an ESR signal typical of Ti\(^{3+}\) with octahedral symmetry (\(g_\parallel = 1.971\) and \(g_\perp = 1.907\)) which was also found after CO reduction. CO reduction of TAPO-5 also gave an ESR signal with a rhombic g tensor, which is different from that of Ti\(^{3+}\) formed by \(\gamma\)-irradiation. These differences were related to additional coordination of tetrahedral framework titanium with CO molecules. Simulation of \(^{31}\)P ESEM spectra for Ti\(^{3+}\) ions in TAPO-5 showed one phosphorus atom at 0.39 nm and two phosphorus atoms at 0.48 nm, which is consistent with titanium substitution for framework phosphorus. Prakash et al (1999) also found that some Ti\(^{4+}\) was reduced to paramagnetic Ti\(^{3+}\) by \(\gamma\)-irradiation and CO reduction in TAPO-11, TAPO-31 and TAPO-36. ESR parameters confirmed Ti\(^{3+}\) formation but do not clearly confirmed the tetrahedral environment. The \(^{31}\)P and \(^{27}\)Al ESEM spectra for Ti\(^{3+}\) ions in the three TAPO structures provided evidence for substitution of titanium into the phosphorus site of AlPO\(_4\) frameworks.

The presence of redox Ti\(^{4+}/Ti^{3+}\) couples in TAPO materials is still controversial. Venkatathri and Shetty (2006) confirmed the isomorphous substitution of Ti\(^{3+}\) in AlPO\(_4\) framework from ESR and \(^{31}\)P MAS NMR spectra. UV-Vis and XPS spectra revealed partial oxidation of framework Ti\(^{3+}\) into Ti\(^{4+}\) in the calcined TAPO-31 and thus the presence of redox centres in the products (Venkatathri and Shetty 2006).
The diffuse reflectance UV-Vis and photoluminescence study of titanosilsesquioxane dimer molecular compound and Ti-MCM-41 catalyst with a well defined coordination of titanium ions were useful (Gianotti et al 2003) to clarify the local environment of Ti\(^{4+}\) ions in TAPO-34 and TAPSO-34 materials. In these samples a significant fraction of Ti\(^{4+}\) ions is in the framework positions, both as isolated tetrahedral centres (absorption bands at 210 nm and emission bands at 425 and 480 nm) and in dimeric Ti–O–Ti species (absorption band at 240 nm). Around 20% of the overall amount of titanium used in the synthesis gel was present as TiO\(_2\) like extra phase (absorption band at 280 nm) as evidenced by Raman spectroscopy.

The isomorphous substitution of Ti ions in TAPO-5 and TAPO-11 framework was also confirmed by the decrease in the unit cell constants upon substitution of titanium (Ulagappan and Krishnasamy 1996). Zahedi-Niaki et al (2002) studied the environment of titanium in TAPO-5, -11, -31 and -36 using XANES and XPS techniques. The XPS results revealed that three different titanium species with Ti in isolated tetrahedral, isolated pentahedral and polymeric TiO\(_x\) in octahedral environments existed on the surface of all TAPO samples. The XANES results showed that the titanium species in TAPO-36 and TAPO-5 possess different environment compared to that in TAPO-11 and TAPO-31.

Akolekar and Ryoo (1996) also studied TAPO-5 material using XPS, EXAFS and \(^{31}\)P MAS NMR. TAPO-5 showed significant catalytic activity in the liquid phase conversion of cyclohexanol. The catalytic activity of AlPO-5 samples increased with Ti concentration in the AlPO framework. NMR investigation indicated the presence of Al and P in tetrahedral environment in the molecular sieves. The overall information obtained from the XAFS data indicated that Ti was incorporated in the framework of TAPO-5 materials. Kim et al (2000) employed IR and UV-Vis spectroscopies
on TAPO-5 and TAPO-11 samples in order to determine the substitution of Ti into AlPO₄ frameworks. It was found that Ti atoms are mainly substituting for P atoms in these two structures. UV-Vis was also employed with XANES spectroscopic technique to prove the isomorphous substitution of titanium in VPI-5 framework (Tušar et al. 2001).

Gianotti et al. (2003a) compared meso-Ti-AlPO with Ti grafted MCM-41 using FT-IR spectroscopy with ammonia as probe molecule. They found that the acidic properties of these materials are intermediate between silica and zeolites which can be useful for catalytic reactions where mild acidity is necessary. DRS-UV-Vis spectroscopy also revealed that tetrahedral Ti⁺⁺ sites, the active centres for many selective oxidation reactions, were present in meso-Ti-AlPO (Gianotti et al. 2003a).

Many analogies for the Ti structure in TAPOs can be found in silica-based catalysts. The EXAFS studies on Ti-silicalite revealed the four fold coordination of titanium and increased the coordination sphere upon adsorption of ligands (H₂O and NH₃) (Bordiga et al. 1994). Chang and Kevan (2002a) evidenced the presence of tetrahedral framework sites for titanium in Ti-MCM-48 and a non-framework site for titanium in Ti-AlMCM-48 using ESR study. Gianotti et al. (2007) studied the local coordination, acidity and accessibility of titanium in various Ti⁺⁺ grafted materials such as Ti-MCM-41, Ti-SiO₂ Aerosil and Ti-SiO₂ Davison using FT-IR and DRS-UV-Vis spectrocopies with probe molecules (CO and acetonitrile). Acetonitrile (and its deuteriated form) was found to be a useful molecular probe to monitor the accessibility of Ti⁺⁺ sites and their quantification. The use of this molecule could provide necessary information for the evaluation of catalytic activity in Ti⁺⁺ containing catalyst. However, CD₃CN is limited in distinguishing Ti⁺⁺ sites with a different coordination. Otherwise, carbon monoxide helps in detecting different coordination environment and connectivities of Ti⁺⁺ active sites (Gianotti et al. 2007).
1.9 SCOPE AND OBJECTIVES OF THE PRESENT STUDY

The incorporation of one or more transition metal ions into AlPO$_4$ framework has gained considerable attention because of the reactivity in selective oxidation reactions because of their redox behaviour and potential bifunctionality (Brønsted sites). A wide array of amines can be used as structure directing agents for the preparation of microporous AlPOs. AlPO-5 and AlPO-11, not template specific, can be synthesized using more than one template.

The framework substitution of Co and Fe in the AlPO$_4$s structures is generally accepted to involve substitution of divalent cation for Al$^{3+}$ ions, while the framework substitution of tetravalent V and Ti in AlPOs is more complex and still controversial. The rich literature about Co, Fe, V and Ti substituted AlPOs reviewed here are reporting about their catalytic performances and their characterization. The main results obtained by various spectroscopic techniques such as DRS-UV-Vis, FT-IR, ESR, ESEM, NMR, Mössbauer and XAS spectroscopies are resumed. These techniques were employed for better understanding about the surface chemistry and nature (location, isomorphous substitution, coordination, oxidation state and redox ability) of the transition metal ions (Co, V, Fe and Ti) in AlPO$_4$-5 and AlPO$_4$-11 framework structure.

In this work two divalent (Fe and Co) and two tetravalent (V and Ti) transition metal ions were inserted by hydrothermal synthesis in AlPO-5 and AlPO-11 open frameworks. General characterization was performed to check the purity and crystallinity of the desired phase, its surface area, morphology and chemical composition. In depth spectroscopic techniques were employed to understand the accessibility, redox ability, coordination and oxidation state of the metal ions in CoAPO-5, CoAPO-11, VAPO-5, VAPO-11, FeAPO-5 and TAPO-5 for specific catalytic application and to design novel catalysts.
Suitable complementary spectroscopic techniques were selected to reach reliable conclusions about the nature of redox sites. The general characterization of the samples was performed using XRD, BET, TEM, SEM and EDX analysis. Raman spectra was also measured in some specific cases. DRS-UV-Vis and FT-IR spectroscopic techniques with probe molecules such as CO, NO, CD$_3$CN and NH$_3$ were used to understand the nature and surface chemistry of the above mentioned materials.

The main objectives of the present investigation are

i) Hydrothermal synthesis of CoAPO-5 and CoAPO-11 using aluminium isopropoxide for CoAPO-5, aluminium hydroxide for CoAPO-11, phosphoric acid and cobalt nitrate as the sources for Al, P and Co respectively. Triethylamine for CoAPO-5 and dipropylamine for CoAPO-11 as the structure directing agent.

ii) General characterization of the above material using XRD, BET, SEM and TEM with EDX analysis.

iii) Spectroscopic characterization of CoAPO-5 and CoAPO-11 by DRS-UV-Vis and FT-IR spectroscopic techniques with CO and NO as probe molecules.

iv) Hydrothermal synthesis of VAPO-5 and VAPO-11 using aluminium isopropoxide for VAPO-5, aluminium hydroxide for VAPO-11, phosphoric acid and vanadyl sulfate as the sources for Al, P and V respectively. Triethylamine for VAPO-5 and dipropylamine for VAPO-11 as the structure directing agent.

v) General characterization of VAPO-5 and VAPO-11 materials using XRD, BET and SEM with EDX analysis.
vi) Spectroscopic characterization of VAPO-5 and VAPO-11 by DRS-UV-Vis and FT-IR spectroscopic techniques with CO and NO as probe molecules and also Raman spectroscopy.

vii) Hydrothermal synthesis of FeAPO-5 using aluminium hydroxide, phosphoric acid and iron acetate as the sources for Al, P and Ti respectively. Triethylamine as the structure directing agent.

viii) General characterization of FeAPO-5 using XRD, BET and SEM with EDX analysis.

ix) Spectroscopic characterization of FeAPO-5 using DRS-UV-Vis and FT-IR spectroscopic techniques with CO and NO as probe molecules.

x) Hydrothermal synthesis of TAPO-5 using aluminium hydroxide, phosphoric acid and titanium (IV) isopropoxide as the sources for Al, P and Ti respectively. Triethylamine as the structure directing agent.

xi) General characterization of TAPO-5 using XRD, BET and SEM with EDX analysis.

xii) Spectroscopic characterization of TAPO-5 using DRS-UV-Vis and FT-IR spectroscopic techniques with CO, CD$_3$CN and NH$_3$ as probe molecules.

xiii) Comparing the behaviour of low oxidation state metal ions (Co$^{2+}$ and Fe$^{2+}$) and high oxidation state metal ions (V$^{4+}$ and Ti$^{4+}$) in two different framework types (large pore AlPO-5 and medium pore AlPO-11).
1.10 CHARACTERISATION STRATEGIES FOLLOWED

The location and structure of the reactive metal ion is of considerable importance to understand the chemistry of heterogeneous catalysts. In particular, the interaction of such active metal ion sites with different adsorbates and reactants helps to understand catalysis at molecular level. A sufficiently good understanding of the local structure of catalytically active metal species in microporous materials can potentially enable optimization and control of the catalytic activity of such systems. A series of suitable complementary characterization techniques such as X-ray Diffraction (XRD), surface area analysis employing the Brunauer-Emmett-Teller (BET) equation, transmission electron microscope (TEM), scanning electron microscope (SEM), energy dispersive X-ray analysis (EDX) and Raman spectroscopy were applied together with diffuse reflectance UV-Visible spectroscopy (UV-Vis) and Fourier transform infrared (FT-IR) spectroscopy associated with the use of probe molecules.

1.11 SPECTROSCOPIC TECHNIQUES

A series of important characteristics of solids, e.g., their adsorptive and catalytic, optical and electrical properties, etc., depend on their surfaces. Therefore, surface science is one of the most important branches of modern physics and chemistry involving a wide range of methods (Madey and Yates 1987, Milling 1999 and Suëtaka and Yates 1995). To describe the state and properties of a given surface one should normally perform in depth investigations of well defined single crystal faces by XPS, LEED, etc. However, most materials of practical importance are powders and single crystals are not available for many of them. Furthermore, the presence of a large number of crystal lattice defects (including edges, corners and steps) (Madey and Yates 1987, Milling 1999 and Rudzinski and Everett 1991) in the dispersed materials (such as oxides) presupposes a large difference between

When oxides are concerned the metal ions on the various crystal planes differ in their coordination states which cause differences in their adsorptive properties and catalytic activities (Dąbrowski and Tertykh 1996, Hadjiivanov and Klissurski 1996, Rudzinski and Everett 1991, Wingrave 2001 and Zecchina et al 2001). In the case of molecular sieves, the open framework microporous structure is responsible for the high surface area so that all the metal ions are accessible to reactants molecules. This explains why the methodologies classically employed to study surface of oxides could be applied with success to the study of zeolites and zeotypes.

Infrared (IR) spectroscopy is uniquely valuable for investigation of powder samples. It gives direct information about the chemical nature of surface or adsorbed species as well as about their structures and strengths of the chemical bonds (Madey and Yates 1987 and Suëtaka and Yates 1995). The IR spectrum of an activated sample gives some direct information about the material (Davydov 1984 and Suëtaka and Yates 1995). In the most favorable cases, general conclusions can be drawn concerning the surface hydroxyl groups and some stable surface species such as sulfates, oxo-groups, etc. Diffuse reflectance UV-Vis spectroscopy (DRS) is also useful technique to monitor the coordination and oxidation state of the metal ions in the porous materials.

1.11.1 **Fourier Transform Infrared (FT-IR) Spectroscopy**

Since 1905, when Coblentz obtained the first IR spectrum, vibrational spectroscopy has become an important analytical tool in research. By 1940, there was a large body of knowledge concerning IR spectroscopy
(Griffiths 1992, Miller 1992 and Wilks 1992). Three programs of great importance during World War II provided the impetus to begin the manufacture of IR instruments viz., the synthetic rubber program, largely a US project, the production of aviation fuel, primarily a UK project, and the penicillin program, a joint US–UK endeavour. In 1943, a new technique was introduced for solid samples with Nujol as a mulling agent and 9 years later KBr was used for solid discs. In 1954, the analysis of samples in a matrix of liquid argon was introduced. Finally, attenuated total reflection (ATR) was developed independently by Fahrenfort and Harrick between 1959 and 1960. It has been especially useful for thick samples, strong absorbing samples and surface studies. In the 1960s, the era of Fourier transform IR (FT-IR) began. It was possible due to the application of a new optic element (the Michelson interferometer), the development and miniaturization of lasers, the introduction of algorithm for fast Fourier transform (FFT) and the use of triglycine sulphate (TGS) pyroelectric bolometer. IR was probably the first vibrational technique to be applied to the analysis of adsorbates on well defined surfaces. Terenin and Kasparov during the early 1940s made the first attempt to employ IR in adsorption studies. They studied the absorption spectrum of ammonia adsorbed on a silica aerogel containing dispersed iron. The work was continued by Terenin and his collaborators after the second world war. Carbon monoxide chemisorbed on metals and metal oxides supported on silica or alumina powder has been the subject of extensive studies by Eischens et al (1954).

After nearly 50 years of intensive application, IR remains the most widely used and usually most effective spectroscopic method for characterisation of the surface chemistry of heterogeneous catalysts. IR always played an important role in characterisation of heterogeneous catalysts, as it permits direct monitoring of the interaction between adsorbed molecules and the catalysts. The goals of catalytic research are varied.
Complete understanding of catalytic reaction mechanisms including the nature of adsorbed intermediates is of course, highly desirable. Catalysis is however primarily an applied science and as such should reasonably be expected to provide major assistance in reaching the goals of better catalysts and improved catalytic processes, from a better fundamental understanding of catalyst surface chemistry.

1.11.2 DRS-UV-Vis Spectroscopy

Identifying and quantifying oxidation states and coordination environment of transition metal ions (TMIs) in porous materials is crucial for understanding their chemistry and catalytic action. Various spectroscopic techniques such as X-ray photoelectron spectroscopy (XPS), electron spin resonance (ESR) and Raman spectroscopy are available to perform this task. But the heterogeneous nature of porous materials and the simultaneous occurrence of several oxidation states of (incorporated or supported) TMIs make the analysis difficult, and in most cases, only qualitative information is obtained. Diffuse reflectance spectroscopy in the ultra-violet, visible and near-infrared region is, in principle, the most versatile spectroscopic technique, as both d-d and charge transfer (CT) transitions can be probed (Kortum 1969 and Schoonheydt 1984). One of the advantages of DRS-UV-Vis spectroscopy is that the obtained information is directly chemical since the outer shell electrons are probed. Furthermore, the DRS technique can be used under in situ condition and is quantitative in nature. The main disadvantage is that diffuse reflectance spectra are complex and usually encompasses several bands.

DRS is a particularly suitable technique for studying the speciation of supported or incorporated TMIs because it measures both their d-d transitions and charge transfer bands. It is clear that the number, wavelength and intensity of d-d bands depend on the oxidation state and
coordination environment (octahedral, tetrahedral, etc.). Among the spectral region, 200 - 2500 nm (covering ultra violet, visible and near infrared regions), 200 - 800 nm region is of special interest for studying the TMIs in porous materials while 800 - 2500 nm region gives information about vibrational modes of surface species or adsorbed molecules. DRS-UV-Vis has been most often considered as a tool for qualitative characterization of supported catalysts (Weckhuysen et al 1998 and 2000a) or modified zeolites (Blatter et al 1994 and Dzwigaj et al 1998). Gianotti et al (1999) used DRS-UV-Vis associated with the use of probe molecules as a supporting tool to other spectroscopic techniques.

1.12 USE OF MOLECULAR PROBES

IR spectrum of the sample is “blind” with respect to the presence of coordinatively unsaturated surface (cus) ions, which are decisive for the catalytic properties. IR spectroscopy also gives rather poor information about the acidity of surface hydroxyl groups which are of great importance for the surface properties. Furthermore, no discrimination between bulk and surface species can be made. Possible information about the accessibility of the metal sites using DRS-UV-Vis spectrum of powdered porous materials would be an added advantage for better understanding of the surface properties. These problems are solved by the use of probe molecules (Davydov 1984, Knözinger and Huber 1998, Kustav 1997, Madey and Yates 1987 and Suëtaka and Yates 1995), substances that interact with the surface; the alteration of the spectral features as a result of adsorption can provide indirect information about the properties, location, concentration, etc of the surface sites.

The ideal probe molecule should meet the following criteria (Davydov 1984, Knözinger and Huber 1998 and Kustav 1997):

- The functional group or the atom through which the molecule bonded to the surface should be well known.
- The probe molecules should occupy the same kind of sites during adsorption on different oxides and form complexes with similar structures.

- Adsorption complexes should be stable enough to allow characterization.

- The probe molecules should have spectral parameters that are sensitive to the state of the sites on which they are adsorbed.

- The informative absorption bands of the surface species should be in the regions in which the sample is transparent.

- The extinction coefficients of the informative bands must be high.

- The probe molecule should not cause any chemical modification of the surface.

- The probe molecule should be small enough to avoid steric hindrance of adsorption.

Probe molecules may be classified according to their abilities to determine (i) surface acidic sites, (ii) surface basic sites and (iii) oxygen vacancies. Weak, intermediate and/or strong bases can be used as probe molecules. However, the interactions of weak and intermediate bases with catalytic surface sites are preferred because they are much more specific than strong bases. These techniques are also powerful tools to elucidate the local coordination, dispersion and accessibility of the metal active centers present in different porous materials.
1.12.1 Carbon Monoxide as a Probe Molecule

IR spectroscopy of adsorbed CO as a probe molecule is a very powerful technique for characterization. Eischens et al (1954) published the first work describing IR spectra of adsorbed species i.e. CO on silica supported metals. This is a powerful stimulus for many researchers to study CO adsorption on supported species, oxide surfaces and porous materials. The use of CO as a probe molecule is based on its non reactive adsorption. In this case the oxidation and coordination states of the metal ions may be determined by the spectral behavior, stability and other characteristics of the carbonyls formed. However, low-temperature CO adsorption has also found increasing application for the determination of acid strength of surface hydroxyl groups. In this case the shift of O–H stretching mode provides additional information.

The vibrational spectrum of CO is simple and strongly affected by adsorption. The $\nu(\text{C–O})$ stretching vibration is sensitive to the strength of the bond formed with the surface. The extinction coefficient of CO is high. It depends, however, on the nature of the bond with the surface. In addition, the CO molecule is small and its adsorption is not hindered by steric interactions. Therefore, CO is one of the most frequently used probe molecules in IR spectroscopy.

Interaction of CO can lead to the formation of different species (carbonyls, isocarbonyls, carbonates, bicarbonates, carbonites, etc). The linear coordination of CO with the carbon end of CO is the most typical and important for practical applications. Apart from linear C-bonded carbonyls and polycarbonyls, formation of bridged CO, O-bonded CO and tilted CO are also possible during the adsorption studies on oxide surfaces and porous materials. Variations of C-O stretching frequency of $\text{M}^{n+}$-CO species are
typically observed in the spectral region between 2245 and 2000 cm$^{-1}$. The IR frequency of CO in the gas phase is 2143.16 cm$^{-1}$ (Nakamoto 1970).

There are many factors affecting the stretching frequency of CO after adsorption. Some are not very important and do not depend on the nature of the coordination bond. Thus, immobilization of CO slightly shifts the CO modes. However, the weak contribution of this effect can be judged from the frequency of physically adsorbed CO at about 2138 cm$^{-1}$. A simple mechanical coupling between C–O and M–C modes could also have a negligible effect on the CO stretching (Knözinger and Huber 1998). The variations of the electrostatic, $\sigma$ and $\pi$ contributions to the bonding of CO in $\text{M}^{\text{uo}}$–CO species are the most important for the shift of its stretching frequency. Generally, the electrostatic interaction and the $\sigma$ bond cause positive frequency shifts and the $\pi$ bond causes negative frequency shifts.

CO can be used in combination with other probe molecules such as CO+NO mixtures to obtain more information from the IR spectra. The use of $^{13}$CO, however, deserves a special consideration. When multiple carbonyls are to be identified isotopic mixtures should be used. Sometimes the polycarbonyls are very stable. In this case, if $^{12}$CO is adsorbed first and then $^{13}$CO introduced, mixed species may not form at ambient temperature. To measure the static and dynamic shifts adsorption of isotopic mixtures (enriched in one of the components) is also recommended.

1.12.2 Nitrogen Monoxide as a Probe Molecule

Although CO is the most widely used probe molecule, in some cases other probes are more useful and informative for specific studies. NO is also a powerful (strong) probe molecule to study different surface species in porous materials. Like CO, it can provide a wealth of information on the nature and properties of adsorption sites on the samples investigated. IR spectroscopy of
adsorbed NO as a probe molecule is also a very informative technique for characterization of porous materials.

NO molecule has three electron pairs occupying bonding orbitals and one unpaired electron situated in an antibonding orbital (Ahmetov 1985). As a result, the N-O bond order is 2.5 and the N-O stretching frequency is 1876 cm\(^{-1}\). Another electron pair is situated on the 5\(\sigma\) weakly antibonding orbital and makes NO an electron donor (i.e., a weak Lewis base). Coordination of the NO molecule to a Lewis acid via the nitrogen atom is accompanied by a partial charge transfer from the 5\(\sigma\) orbital and an increase in the bond order just as in the case of CO. Formation of a \(\pi\)-back bond, although not so easy as with CO, is also possible, and this results in a decrease in the N-O stretching modes. The vibration frequencies of different surface nitrosyls absorb in a wide spectral range of 1966 – 1710 cm\(^{-1}\).

There are many IR studies using NO adsorption on different surfaces. These works have been inspired by two facts (1) use of NO as a probe molecule and (2) the attempts made to understand the mechanisms of some catalytic reactions involving NO such as NO decomposition, NO+CO reaction and SCR of NO\(_x\) by ammonia. For example, in the determination of the oxidation state of vanadium on vanadia–titania catalysts, NO is more useful. Although the carbonyl bands for \(\text{V}^{4+}\text{–CO}\), \(\text{V}^{3+}\text{–CO}\) and \(\text{Ti}^{4+}\text{–CO}\) species almost coincide (Concepcion et al 1999a), the fact that NO forms nitrosylic complexes with \(\text{V}^{n+}\) but not with \(\text{Ti}^{4+}\) allows the effective use of NO as a probe molecule (Hadjivanov et al 2000). Another promising and growing approach is the use of NO as co-adsorbates like NO+O\(_2\), NO+CO, etc.

### 1.12.3 Other Probe Molecules

Intermediate (CD\(_3\)CN) (Bonino et al 2003 and Pelmenschikov et al 1993) and strong (NH\(_3\)) (Zecchina et al 1997) probe molecules are also used
to monitor the nature of the metal ion sites. However, the interaction of weak and intermediate bases with catalytic surface sites is preferred because they are much more specific than strong bases. Acetonitrile appears an attractive probe for surface acidity since it will allow two kinds of vibrational studies. When interacting with surface acid sites, both the OH frequencies of a Brønsted site and the acetonitrile frequency $\nu$(CN) will shift with respect to the molecule in the liquid phase which is due to the interaction of the electron lone pair located on nitrogen atom of CH$_3$CN with the acid sites. This makes acetonitrile an interesting probe for both Lewis and Brønsted acidity. The deuterated form, CD$_3$CN instead of CH$_3$CN is also employed in order to avoid the Fermi resonance effect between $\nu$(CN) vibration and the combination mode $\delta$(CH$_3$) + $\nu$(CC) (Angell and Howell 1969, Sempels and Rouxhet 1976 and Venkatesvarlu 1951).

Ammonia, being a strong basic ligand, is also often used as a molecular probe to study the acidity of hydroxyl groups in oxide and porous materials forming ammonium ions with medium to strong Brønsted sites (Zecchina et al 1997). IR spectroscopy of $\nu$(NH) modes of structurally simple ammonium ions, although basically very simple, is actually made very complicated by the presence of several combination bands of unusual intensity and by the presence of multitude of Fermi resonance effects. Still NH$_3$ is used widely to monitor the nature of Lewis and Brønsted sites and can directly interact with the metal centres giving information about their coordination sphere (Astorino et al 1995, Bordiga et al 1994, Keshavaraja et al 1995, Klaas et al 1997, Le Noc et al 1996, Luan et al 1997 and Trong On et al 1995).

1.13 POSSIBLE INFORMATION OBTAINED

In the ideal case, the information that one can obtain by using probe molecules is as follows: oxidation state, coordination state, Lewis acidity of
the cations on the surface, Brønsted acidity of the surface hydroxyl groups, position of the cations on flat planes or other surface structures, position of the supported active phase, surface phase analysis, existence of strong oxidizing agents on the surface, existence of strongly basic oxygen anions. There is still disagreement about some basic questions such as the determination of the oxidation states of some cations.