Sol–gel processing of phosphonate-based organic–inorganic hybrid materials

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The preparation by sol–gel like methods of organic–inorganic hybrid materials based on phosphonate coupling molecules is briefly reviewed, focussing on porous materials. The structure of the materials, the reactions involved and the variety of precursors and templates that have been used are discussed. The potential applications of porous phosphonate-based hybrid materials are also presented.

1. Introduction

Organic–inorganic hybrid materials aim at combining the properties of organic and inorganic compounds in a single, new material.1–4 A wide class of hybrid materials involves strong ionicovalent bonding of organic and inorganic components via “coupling molecules”, allowing the anchoring of organic groups either to an inorganic substrate (surface modification) or to an inorganic network (sol–gel processing).5

The best known coupling molecules are organoalkoxysilanes, which are unavoidable for the sol–gel synthesis of silica-based hybrids or polysilsesquioxane hybrids.2,4,6 In the case of metal alkoxides, coupling via carboxylate, aminoalcohols, or β-diketone groups has been extensively studied.7 The use of organophosphorus coupling molecules such as phosphonic acids in the sol–gel processing of porous hybrid materials is relatively recent.

Actually, crystalline metal phosphonate form a wide class of hybrid materials which has been widely studied since the first report in 1978 of Alberti and coworkers8 on the preparation of Zr alkyl and phenyl phosphonates, Zr(RPO3)2. However, in the case of simple phosphonic acids, metal phosphonates usually adopt layered structures, with no interlayer porosity.9,10 Conversely, if the P/M ratio differs from the ideal one5,11 or if polyphosphonates are used, the formation of a crystalline layered material is prevented and porous hybrid materials are easily obtained.11–14

In 1998, Vieux and co-workers proposed a 2-step sol–gel process to prepare amorphous ZrO2- and TiO2-phenylphosphonate hybrid materials. The first step involved the condensation of a phosphonic acid with an excess of metal alkoxide (compared to the stoichiometry for a layered phosphonate) under anhydrous conditions to form M–O–P bonds, followed in the second step by the hydrolysis-condensation of remaining metal alkoxide groups to form M–O–M bonds.11,13,16

Since this pioneering work, several groups have been exploring the sol–gel synthesis of porous hybrid materials starting from phosphonate coupling molecules and metal (or silicon) precursors.

This concise review presents an overview of the sol–gel synthesis of hybrid materials involving phosphonate coupling molecules, either oxide-phosphonate materials or metal phosphonates involving polyphosphonic acids.

Layered metal phosphonates and bisphosphonates have been amply reviewed,9,10 and these materials will not be further discussed. Similarly, recent review articles have recently been published on hybrid materials obtained by surface modification with phosphonic acids, and these materials are not in the scope of the present article.17–19

In the first part we discuss the structure of phosphonate-based hybrid materials, then we present the precursors, sol–gel chemistry, and templates involved in their synthesis. Finally, in the third part we briefly present the main fields of application.

2. Structure of hybrid phosphonate-based hybrid materials

The common structural feature in phosphonate-based hybrid materials is the presence of M–O–P bridges, which result from condensation reactions (see part 3) and coordination of the phosphonyl oxygen to metal atoms.

The two main parameters governing the structure of phosphonate-based hybrid materials are i) the P/M ratio, and ii) the nature of the phosphonic acid coupling molecule (mono-, bis-, or multiphosphonic acid).

For instance, tetravalent metal phosphonates (M = Ti, Zr, etc.) usually feature [RPO3/2]2− tetrahedra and [MO6/2]4+ octahedra connected through M–O–P bonds only [Scheme 1(b)], and the ideal P/M ratio is 2:

$$2\text{RPO}(\text{OH})_2 + \text{MX}_4 \rightarrow \text{M}(\text{RPO}_3)_2 + 4\text{HX}$$

In the case of monophosphonates and some bisphosphonates, these materials usually adopt layered structures, with no interlayer porosity.9,10 However, if the P/M ratio differs from the ideal one and/or if polyphosphonates (2 or more phosphonate groups) are used, the formation of a layered material may be prevented and porous hybrid materials can be obtained (Scheme 1).14

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Moreover, the structural units present in hybrid materials derived from multiphosphonic acids can be different from the classical ones. Thus, Yuan et al. reported the formation of mesoporous amorphous or crystalline metal-phosphonate materials based on the hydrothermal reaction of ethylenediamine tetra(methylene phosphonic acid) (compound 5, Scheme 2) with metal chloride precursors in the presence of non-ionic surfactants, at pH 4.20. According to FTIR and XPS studies, in the case of Ti these materials featured only P–O–Ti bonds and possibly residual Ti–OH groups. The ideal P/Ti ratio for these materials (and other metal phosphonate) is proposed to be 4/3, corresponding to \([\text{RP}^+\text{O}_3\text{Ti}^3\text{O}^\text{−}]\) tetrahedra by analogy with the structural units in AlPO materials. Such a structure requires the presence of counter anions, to ensure electroneutrality:

\[
\text{R}^{2}\text{PO}^{n}\text{H}_2^{n−} + 3/4n \text{TiCl}_4 + 2n \text{H}_2\text{O} \\
\rightarrow \text{R}^{(\text{P}^{+}\text{O}_3\text{Ti}^{3}\text{O}^{−})^n} + 3n \text{Cl}^{−} + 2n \text{H}_3\text{O}^{+}
\]

When the P/M ratio is lower than the ideal one (excess of metal precursor), metal oxide-phosphonate nanocomposite materials are formed [Scheme 1(a)], featuring a network of M–O–P and M–O–M bridges (and residual M–OH groups).11–13,23–25

When the P/M ratio is higher than the ideal one (excess of phosphonic acid precursor), materials displaying large amounts of un-condensed P–OH (or P–ONa) groups are obtained [Scheme 1(d)].26–31 Yuan et al. proposed to increase the amount of residual P–OH groups by “protecting” them with alkyl amines.32

The structure of phosphonate-based hybrid materials has been extensively studied by various spectroscopic methods, such as FTIR11,32 and X-ray photoelectron spectroscopies33 as well as solid-state NMR spectroscopy (notably33P11,33 and 17O34). All of these methods are useful to qualitatively evidence the presence of M–O–P bridges and of residual M–OH, P–OH and P=O groups. In addition, 17O MAS NMR allows the quantification of the different sites. However, the natural abundance of 17O is very low and the preparation of 17O-enriched phosphonic acids is mandatory.34

3. Sol–gel chemistry of phosphonate-based hybrid materials

The sol–gel synthesis of phosphonate-based hybrid materials involves the reaction of metal (or silicon35) precursors with phosphonate coupling molecules, in aqueous or anhydrous medium, with or without a templating agent (Table 1).

3.1 Phosphonate coupling molecules

Phosphonate coupling molecules are usually phosphonic acids, or phosphonate sodium or ammonium salts. Silylated esters can also be used in non-aqueous medium.11 A wide range of phos-
phonic, bisphosphonic or polyphosphonic acids (and derivatives) featuring various organic groups has been used (Scheme 2).

### 3.2 Metal precursors

As shown in Table 1, metal precursors are usually metal alkoxides or metal chlorides, and in some cases metal oxychlorides (ZrOCl$_2$) or oxoalkoxides [VO(OiPr)$_3$]. El Haskouri and co-workers used an aluminium alkoxide reacted with 2,2′,2′′-nitrilotriethanol (triethanolamine) to form aluminium atrane complexes, in order to lower reaction rates and improve the dispersion of phosphonate units.40) Similarly, when TiCl$_4$ is dissolved in ethanol, the true precursors are most likely a mixture of less reactive titanium oxochloroethoxides.

The water solubility of metal phosphonates is known to decrease with the valency of the metal: four-valent metal phosphonates are practically unsoluble, three-valent phosphonates are more soluble, while divalent phosphonates are usually soluble in slightly acidic media, and all monovalent phosphonates are highly soluble.9) Accordingly, most examples of phosphonate-based hybrid materials concern tetravalent metals (Ti, Zr).

### 3.3 Reactions involved

The M–O–P bridges in phosphonate-based hybrid materials result from condensation reactions and from the coordination of the phosphoryl oxygen to metal atoms. These reactions can take place either in non-hydrolytic (or non-aqueous) or hydrolytic conditions.

Under non-hydrolytic conditions,11) the main condensation reaction used is the condensation between a phosphonic acid (or a polyphosphonic acid) and a metal alkoxide, as originally proposed in the synthesis of Zr oxide-phosphonate hybrids:15)

\[
\text{MOR} + \text{P(OR)$_3$} \rightarrow \text{M–O–P + ROH}
\]

Alternatively, bis-trimethylsilylesters RPO(OSiMe$_3$)$_2$, more easily soluble in organic medium, can also be used.11)

\[
\text{M–OR} + \text{P–OH} \rightarrow \text{M–O–P + ROH}
\]

Note that the formation of P–O–P bridges by condensation of P–OH groups does not take place under the mild conditions used

### Table 1. Examples of phosphonate-based hybrid materials derived from the phosphonic acids given in Scheme 2

<table>
<thead>
<tr>
<th>Phosphonic acid*</th>
<th>Metal precursor</th>
<th>Template</th>
<th>Application</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 R = Ph, Vi</td>
<td>Zr(OPr)$_4$; Ti(OPr)$_4$; Al(O(OPr)$_3$)</td>
<td>None</td>
<td>None</td>
<td>11), 15), 23)</td>
</tr>
<tr>
<td>2 R = Me</td>
<td>Al(O(OPr)$_4$)/Ni(CH$_2$CH$_2$OH)$_3$</td>
<td>CTAB</td>
<td>Catalysis</td>
<td>36)</td>
</tr>
<tr>
<td>3 n = 1–3</td>
<td>Al(OPr)$_4$; AlCl$_3$</td>
<td>C$_y$H$_z$nMe$<em>2$Cl; C$</em>{18}$EO$_5$;</td>
<td>None</td>
<td>37–39)</td>
</tr>
<tr>
<td>4 n = 2</td>
<td>Al(O(OPr)$_4$)/Ni(CH$_2$CH$_2$OH)$_3$</td>
<td>CTAB</td>
<td>None</td>
<td>36, 40)</td>
</tr>
<tr>
<td>5 Ti(OBu)$_4$; TiCl$_4$; ZrCl$_2$</td>
<td>None; EO$_2$PO$_3$EO$_2$;</td>
<td>CTAB</td>
<td>Sorption; Catalysis; Ion exchange; Proton conduction</td>
<td>29, 31, 45–47)</td>
</tr>
<tr>
<td>6 ZrCl$_4$; Ti(OBu)$_4$; TiCl$_4$</td>
<td>None;</td>
<td>EO$_2$PO$_3$EO$_2$;</td>
<td>Sorption; Ion exchange</td>
<td>27, 41, 48, 49)</td>
</tr>
<tr>
<td>7 Ti(OBu)$_4$; ZrCl$_2$</td>
<td>None;</td>
<td>EO$_2$PO$_3$EO$_2$;</td>
<td>Sorption</td>
<td>31, 48)</td>
</tr>
<tr>
<td>8 MoCl$_3$</td>
<td>None</td>
<td>Catalysts</td>
<td>50)</td>
<td></td>
</tr>
<tr>
<td>9 Ti(OPr)$_4$; VO(O(OPr)$_3$)</td>
<td>None</td>
<td>Catalysts</td>
<td>12, 13)</td>
<td></td>
</tr>
<tr>
<td>10 Ti(OBu)$_4$; MnCl$_2$; NiCl$_2$</td>
<td>None;</td>
<td>EO$_2$PO$_3$EO$_2$;</td>
<td>Sorption</td>
<td>20, 31, 55–57)</td>
</tr>
<tr>
<td>11 ZrCl$_4$; Ti(OBu)$_4$</td>
<td>None</td>
<td>Ion exchange</td>
<td>Sorption</td>
<td>28, 41, 58, 59)</td>
</tr>
<tr>
<td>12 Ti(OPr)$_4$</td>
<td>None</td>
<td>None</td>
<td>60)</td>
<td></td>
</tr>
</tbody>
</table>

*: refers to the compounds displayed in Scheme 2.
for sol–gel synthesis or even under hydrothermal conditions used to improve condensation degree or organization.

Additionally, if an excess of metal is present, formation of M–O–M oxo bridges also takes place, involving classical hydrolysis and condensation reactions, such as:

\[ 2\text{M-OH} \rightarrow \text{M-O-M} + \text{H}_2\text{O} \]

3.4 Texture of hybrid phosphonate-based hybrid materials

As mentioned above, when the P/M ratio and/or the structure of the phosphonate coupling molecules are not conducive to layered metal phosphonate formation, porous materials are easily obtained, either without templating or in the presence of templates, as recently reviewed by Yuan and coworkers.14,22

In template-free syntheses, porosity results from the voids remaining after evaporation of solvent and by-products. A high degree of condensation of the gel is needed to avoid pore collapse during drying, and hydrothermal treatment is often used to complete condensation reactions.32,54,59 In all cases, the porosity (pore volume and specific surface area) is highly dependent on the synthetic conditions.13,52,62 Small amounts of organic additives (EO30PO34 copolymer or cycloextrin) have been found useful to improve the texture of the hybrid materials.48

Several groups have investigated the templated synthesis of phosphonate-based hybrid materials, using cationic or non-ionic templates. Kimura25-29 and El Haskouri and coworkers30,40 prepared ordered mesoporous Al alkylene bis-phosphonates (compounds 3 in Scheme 2, with n = 1, 2 or 3) using cationic or non-ionic surfactants. More recently, Yuan et al. obtained Zr phosphonate with tunable pore sizes from compound 4 using hydrothermal synthesis in a CTAB–H2O–ethanol system.47 The same group prepared a wide range of periodic mesoporous metal phosphonate (M = Ti, Zr, V, Al) materials derived from compound 9 (Scheme 2), by autoclaving in the presence of surfactants, such as Brij 56, C16EO10 or the triblock copolymer F127.21 In the case of the bis-phosphonic acid 4, cubic mesoporous Ti-phosphonates were obtained using CTAB as a template,45 while Zr-phosphonates with a hierarchically porous texture were synthesized in the presence of triblock copolymer (F127 or P123) using a mild solvent evaporation strategy.46 Mesoporous Zr-phosphonates with a high P/Zr ratio (around 3) and high P-OH content were prepared using phosphonic acids 4, 6 or 9 (Scheme 2) in the presence of CTAB.29,33,63

4. Potential applications

The potential applications of phosphonate-based organic–inorganic hybrid materials arise from their high specific surface area, from the presence of residual acidic P–O–H groups and/or of organic functional groups, and in some cases from properties of the inorganic part. The organic/inorganic functional moieties can be present in the initial hybrid phosphonate material,22 or added by post-modification.57,64,65

As shown in Table 1, the main applications explored up to now are in the fields of sorption, ion-exchange, and catalysis. These materials have also been proposed for various other applications, such as chromatography23 or photocatalysis,20,37,47,51,52 as detailed in recent reviews.14,22

Hybrid materials derived from phosphonate 4, 6, 9, or 10 have been extensively used as heavy metal cation exchangers and sorbents, owing to the possibility of amine, OH, or P–OH groups to bind to metal ions in water solutions.20,22,27,28,133,41-43,45,46,48,51,52,54-56,58,59,66-71 Hybrid materials based on 4, 6, or 9 have also been proposed as sorbents of CO2 gas.23,45,46,48,53,55,56 or of proteins46,68 or of organic compounds.23,72

Another important application is catalysis. Maillet and coworkers24,25 have used the bis-pyridine compound 3 to prepare metal (Ir, Rh) complexes immobilized in titania matrices for high pressure hydrogenation of C–C and C=C bonds or the reduction of ketones.24,25 Vasylyev et al.13 tested vanadium phosphonate materials based on compound 8 in the aerobic oxidation of benzylic alcohols to benzaldehydes. Mesoporous nickel phosphate/phosphonate hybrid microspheres prepared form 4 showed excellent catalytic activity for the reduction by NaBH4 of 4-nitrophenol to 4-aminophenol.53

Hybrid materials featuring a high P–O–H content are promising acidic catalysts.29,50 For instance Zr phosphonates based on compounds 4 or 8 were used as catalysts for the condensation of D-ribose with acetone and methanol,29 or the esterification of acetic acid with ethanol or cyclohexanol.31

Using alendronate (compound 5) as a coupling molecules, Ma et al. prepared a mesoporous dual catalyst with a large number of accessible acidic P–OH and basic NH2 sites, highly active in the cycloaddition between CO2 and azidine.30

5. Conclusions

Although the synthesis of phosphonate-based organic–inorganic hybrid materials by sol–gel methods is relatively recent compared to organosilicon-based hybrids, a wide variety of materials with interesting textures has been prepared. This texture combined with the intrinsic properties of organic or inorganic moieties opens up numerous potential applications, notably in the fields of sorption, ion exchange and (photo) catalysis.

References

17) R. Boissezon, J. Muller, V. Beaugears, S. Monge and J.J.
J. Mater. Chem. 
27) B. Shah and U. Chudasama, 
Indian J. Chem., Sect. A: 
38) T. Kimura, 
33) T.-Y. Ma, X.-J. Zhang, G.-S. Shao, J.-L. Cao and Z.-Y. Yuan, 
ChemSusChem 
22) T.-Y. Ma and Z.-Y. Yuan, 
Chem. Mater. 
24) C. Maillet, P. Janvier, M.-J. Bertrand, T. Praveen and B. Bujoli, 
J. Phys. Chem. C 
14, 4781–4786 (2010). 
34) V. Lafond, C. Gervais, J. Maquet, D. Prochnow, F. Babonneau, 