New Multifunctional Zirconium(IV) Phosphonates Derivatives as Proton Conductors and Catalysts

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Coordination polymers (CPs) based in phosphonic acid display a wide range of metal-coordination modes. Moreover, the existence of acidic P-OH groups in their structure, as well as of others functionalized organic group such as carboxylic or amino groups, together with the presence of coordination and/or lattice water molecules favors the formation of hydrogen bond networks, make them appropriate materials as proton conductors and, therefore, attractive for proton exchange membranes (PEMs) of fuel cells or electrolyzers.[1]

The current interest in metal phosphonates, in particular zirconium derivatives, lies in their properties, such as high chemical and thermal stability and high insolubility. In addition, zirconium phosphonates have also been studied for specific purpose such as catalysis [2], ion exchange and intercalation processes [3], so on.

In this work, we reported the synthesis, characterization and structural determination of three new zirconium phosphonates derived from the phosphonic acids: ***Zr-PNA*** (PNA = 5-(dihydroxyphosphoryl) nicotinic acid), ***Zr-BTMP*** (BTMP = 1,2,3-[phenelyenetris(methylene)]tris-phosphonic acid) and ***Zr-PiPthA*** (PiPthA = 5-(dihydroxyphosphoryl)-isophthalic acid). All zirconium derivatives were synthesized under hydrothermal conditions at 80 ºC in the presence of HF as mineralizing agent.

The crystal structures of ***Zr-PNA*** and ***Zr-BTMP*** have been solved from powder X-ray diffraction data and both solid crystallize in the monoclinic system. ***Zr-PNA*** ($Zr[(O_3P\text{-}NH\text{-}C_5H_3\text{-}COOH)_2F_2]$) shows a 1D structure formed by chains of ZrO_4F_2 octahedra bridged by the phosphonates groups of the ligand, while ***Zr-BTMP*** ($Zr[(O_3PCH_2)(HO_3PCH_2)_2\text{-}C_6H_3]\cdot H_2O$) exhibits a 3D framework formed by double chains of isolated ZrO_6 octahedra bridged by the different phosphonates groups of the ligand.

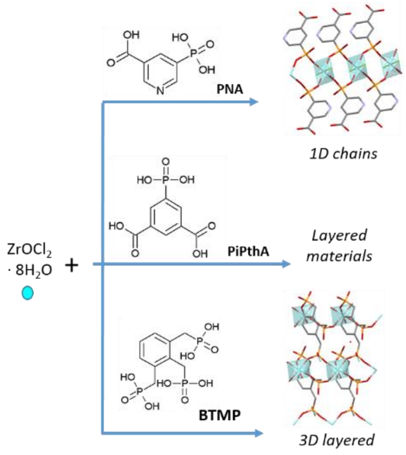

Figure 1. Synthesis and structures of ***Zr-PNA***, ***Zr-PiPthA*** and ***Zr-BTMP***.

Compound ***Zr-PiPthA***, $Zr[(HO_3P\text{-}C_6H_3\text{-}(COO)_2H)_2F_2]\cdot 6H_2O$, crystallizes in an orthorhombic unit cell (a = 21.9306 Å,b = 16.6169 Å, c = 3.6462 Å). Their structural features, proton conductivity and ion exchange properties as well as their catalytic behavior toward the one-pot transformation of furfural to other bio-products reaction will be discussed.

References

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