

POROUS MATERIALS BASED IN LAMINAR AND PILLARED ZIRCONIUM PHOSPHATES FOR THE EFFICIENT STORAGE OF HYDROGEN

Ernesto Brunet, Carlos Cerro, Olga Juanes and Juan Carlos Rodriguez-Ubis
 Department of Organic Chemistry, Faculty of Sciences C-I-207, Universidad Autónoma de Madrid, 28049-Madrid (Spain)
ernesto.brunet@uam.es

Hydrogen is a very appealing energy vector: the release of its energy does not involve the noxious carbon dioxide. Yet, it is becoming a well known fact by our society that two problems must be solved if hydrogen is to be efficient and safely used as the clean energy carrier of the future: *i*) its environmental-friendly production and *ii*) its safe storage and transportation. Although there are already many reasonably useful technical approaches, neither of the two problems is nowadays at a level of resolution which would make the use of hydrogen routinely possible. Besides, the technical solutions to these problems must be quite robust in order to make a smooth transition to the “hydrogen culture” from the actual fossil-fuel civilization, whose economic moguls are far too powerful to be convincingly counterfeited. Therefore, a lot of research is being performed and even new institutions are being created to accomplish the aforementioned double task. Concerning the second one, hydrogen storage (HS) may be attained by at least four main methods: *i*) in high-pressure cylinders, *ii*) as a liquid in cryogenic tanks, *iii*) in ionic or covalent compounds (chemisorption), and *iv*) by *physisorption* in porous matrices.[1] This communication will give a critical quick view of the visible state-of-the art of the latter method (*physisorption*) and report our approach and progress in the use of porous organic-inorganic solids based in Al and Zr and various phosphonates.

A thorough revision of the literature (Figure 1) shows that the materials with very large specific surface areas (the record is well above 3000 m²/g) are not suitable for efficient HS at room temperature and low pressures, as common sense would have been anticipated. The free energy of interaction among the hydrogen molecules and the scarce matter of these systems is very low similarly as it is in an empty cylinder. Therefore, to increase that interaction energy, closer contact H₂-material and thus much smaller pores are needed. It is now considered that a material bearing micropores or even ultramicropores would be more efficient for HS.[2] Many reported materials fall within this category. However, the average HS capacity (A and B in Figure 1) is around 2 wt% (77K and 1 atm) and a barrier of 3-4 wt% appears to be by far insurmountable. The average enthalpy of interaction H₂-material is around 6-7 KJ/mol. It seems clear that higher enthalpies are needed (15-20 KJ/mol) to achieve HS at room temperature and atmospheric pressure. It should be noted that a record enthalpy of interaction (17.5 KJ/mol) was reported in faujasite-type (Mg,Na)-Y zeolite[3] but, unfortunately, the HS was low due to a strong entropic compensation. The existence of ions, specially Li⁺, and/or the presence of metals with open coordination sites in microporous organic-inorganic scaffolds are considered quite favourable features to increase HS.[4] Also, the presence of aromatic moieties in these scaffolds, probably with the idea of building kin

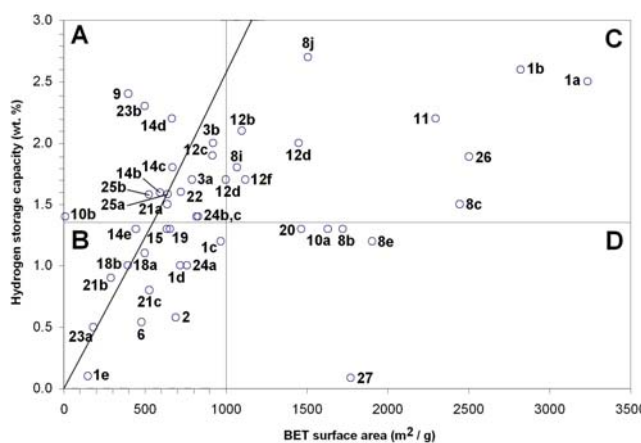


Figure 1

structures to superactivated carbon, graphenes and carbon nanotubes, is also a coveted architectural characteristic.

We are investigating the possibilities that organic-inorganic scaffolds based in phosphonates and Al and Zr have in this field. Although our preliminary results have been only quite modest,[5] we believe that we have a set-up of conceptual and material tools,[6] similar to that reigning organic chemistry, which could lead to the design of an endless number of structures and interesting results. For instance, the use of $\text{Al}_2(\text{HPO}_3)_x$ ($\text{C}_{12}\text{H}_8\text{P}_2\text{O}_6$) $_{1.5-x/2}$ allows the easy control of the HPO_3 /diphenylphosphonate ($\text{C}_{12}\text{H}_8\text{P}_2\text{O}_6$) ratio. The resulting materials displayed a good correlation between wt% HS and the HPO_3 content (UAM-150 \rightarrow 152: cf. Figure 2), probably due to the increasing internal area caused by the increment of latter.[7]

The Zr derivatives, in which we have a larger experience, seem to be even much more flexible. Three phases (α , γ and λ ; Figure 3) of quite different structures are known for Zr phosphates which easily allow the inclusion of a variety of species, comprising various organic components (carboxylic acids, amines, phosphonates, etc), various phosphorous acids and metal ions. Preliminary results in the building of these structures with the phosphonates of Scheme 1 will be reported in this communication.

References

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- [3] Turnés, G.; Llop, M. R.; Otero, C. *J. Mater. Chem.*, **2006**, *16*, 2884-2885.
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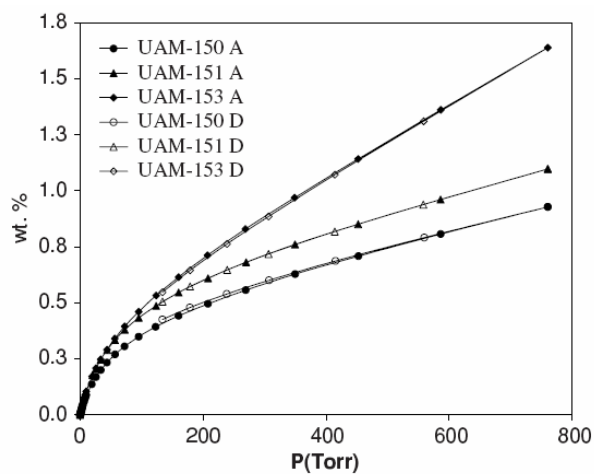


Figure 2

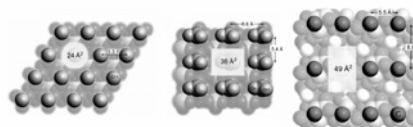
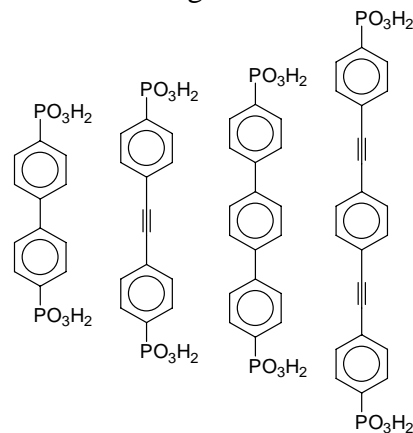


Figure 3



Scheme 1

[7] Brunet, E.; Cerro, C.; Juanes, O.; Rodríguez-Ubis, J.C.; Clearfield, A. *J. Mater Sci.* **2008**, *43*, 1155-1158