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#### Innovative hybrid materials for hydrogen storage

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Given the current environmental problems, renewable energy resources (such as photovoltaics or wind power) are now an absolute necessity. However, the intermittency of these resources in the production of electricity is a key factor and energy storage and efficient energy conversion systems are required. In this context, hydrogen could be used as a vector energy for renewable energy. Indeed, hydrogen can be produced by electrolysis and then the energy contained in this molecule can be released thanks to a fuel cell. But to achieve this, the issue of hydrogen storage needs to be overcome.

Organic molecular crystals, like hydroquinone clathrates, could be promising hydrogen storage materials. Clathrates are supramolecular compounds consisting of a guest molecule (here  $H_2$ ) and cavity-forming host molecules. The formation of hydroquinone (HQ) clathrates with gases such as  $CO_2$ <sup>1</sup> or  $CH_4$ <sup>2</sup> is well known in the literature. But, for hydrogen capture, some important restrictions limit the development of this material, like high pressures and low kinetics of clathrate formation. Han et  $al$ <sup>3</sup> were able to obtain a hydrogen HQ-clathrate by pre-forming a guest-free structure, and then filling it with H2 at 350 bar. Other attempts were done to improve the storage capacity of hydroquinone clathrate, like the addition of  $C_{60}$ <sup>4</sup> but not optimal system has been found to date. The strategy developed in this work consists in the impregnation of hydroquinone inside the micropores of a porous material in order to use the confinement effect both to initiate the formation of the confined clathrates and to improve the kinetics of enclathration. To do so, a novel method of impregnation is developed and tested on several materials of different chemical nature (carbon, polymer, silica) and having various pore size (between 1 and 15 nm). TGA-DSC, Argon porosimetry and MAS-NMR are used for the characterization of the new composites. The impregnation rate of organic crystals can reach up to 35% by mass of the hybrid material. The storage capacity of hydrogen is measured with a magnetic suspension balance. For the case of HQ impregnated in a porous polystyrene-based material, the formation of the HQ clathrate can be reached with cycling the temperature between 0 and 100°C. The storage capacity of the sample increases from 0.1 to 1.3 wt.% per gram of sample (or 7 wt.% per gram of HQ) under 20 bar of  $H_2$  in ten temperature cycles. Moreover, the system is stable at room temperature and  $P = 1$  bar of  $H_2$  with a storage capacity of 5.7wt.% of H<sub>2</sub> per gram of HQ and H<sub>2</sub> can be totally released at  $100^{\circ}$ C. Similar storage capacities are also obtained with other materials such as MCM-41+HQ.

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