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Development of Functional Metal-organic Frameworks (MOFs) for Storing Hydrogen in Para Form

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Abstract

In this work, enrichment of para-hydrogen is performed by flowing ultra-purity hydrogen gas at low temperature (77 K) in the presence of a developed catalyst anchored in a MOF hybrid material. This approach fits within the bigger scope of the development of a novel material-based controllable switch for uptake/release of hydrogen in a storage system. The effect of the tuned dielectric properties of the material was tested against the hydrogen storage capacities.

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1. Introduction

After being studied for decades, effective storage of hydrogen is found to be a tough mission to accomplish. Although acceptable storage capacities have been obtained at 77 K with highly porous adsorbents such as metal-organic frameworks (MOFs), the capacities drop significantly at room temperature due to the weak van der Waals interaction between hydrogen molecules and MOFs [1,2]. The existence of two forms of molecular hydrogen i.e. ortho-hydrogen and para-hydrogen, has been known to physicists and chemists for almost 90 years [3]. As shown in

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Fig. 1, ortho-hydrogen is in a higher energy state than para-hydrogen. The equilibrium mass fractions of ortho-para hydrogen are temperature dependent as described by Eq. (1) [4]:

$$X_p = \frac{X_o}{3} \cdot \frac{1 + 5 \cdot e^{-\frac{86.2}{T}}}{3 \cdot e^{-\frac{2 \cdot 86.2}{T}} + 7 \cdot e^{-\frac{12 \cdot 86.2}{T}}} \tag{1}$$

Where e is the equilibrium concentrations; X_p is the mass fraction of para-hydrogen and X_o is the mass fraction of ortho-hydrogen.

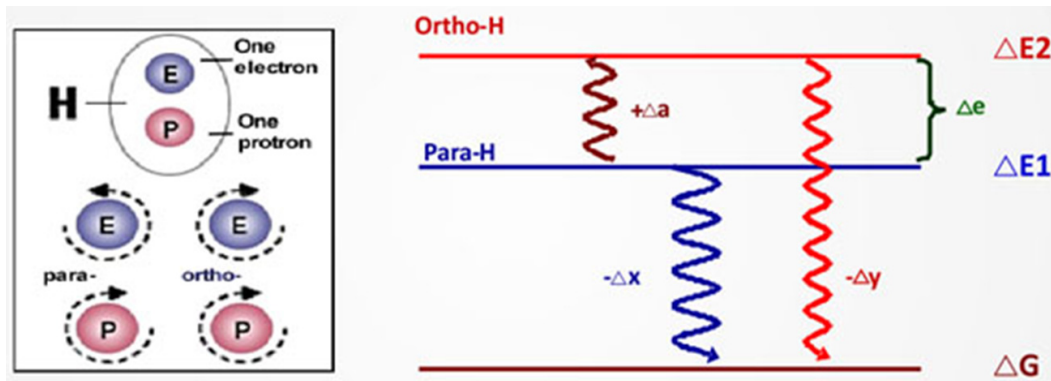


Fig. 1. Ortho-hydrogen and para-hydrogen.

The two forms of hydrogen are transitional in an isolated system but at an extremely slow rate due to violation of symmetry selection rule. Hydrogen at room temperature (300 K) is a mixture of 75% ortho-hydrogen and 25% para-hydrogen, and below room temperature the composition of ortho-para fraction varies. 100% para-hydrogen can be achieved when temperature decreases to 20 K (liquid hydrogen) [5,6]. Such conversion can be promoted in the presence of an engineered solid surface [7], and the catalytic activity of MOF materials have been proved enough to make instantaneous conversion of adsorbed H₂ molecules [8,9]. In practices, higher hydrogen storage capacities can be expected by storing hydrogen in the para form. To enable long-time hydrogen storage, the reversible transition from para-hydrogen to ortho-hydrogen must be prevented in the system. The dielectric coating onto porous materials have been reported to achieve the enhanced hydrogen storage capacity, and the stronger interaction between charged material surface and polarized hydrogen molecules played a positive role [10]. In addition, the interaction of para-hydrogen with paramagnetic catalyst was reported to induce the conversion to ortho-hydrogen [11]. Therefore, steel cylinders with paramagnetic properties are expected to catalyse the conversion rate of para-hydrogen to ortho-hydrogen.

In this work, MIL-101(Cr) or composite materials will be developed first to enrich para-hydrogen by passing extra-pure hydrogen gas through a catalyst bed packed with the developed hybrid materials at liquid nitrogen temperature (77 K). Then, dielectric coating will be put onto MIL-101(Cr) materials to prevent the re-establishment of the room temperature thermal equilibrium, and a cylinder with aluminium liner will be considered to store the enriched para-hydrogen.

2. Materials and methods

2.1. Reagents and Chemicals

Chromium chloride hexahydrate ($\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, Sigma-Aldrich, 99.5+%), terephthalic acid (Sigma-Aldrich, 98%), formic acid (HCOOH , Sigma-Aldrich, 95+%), titanium chloride (TiCl_4 , Sigma-Aldrich, 99%), and N,N-dimethylformamide (DMF, Sigma-Aldrich, 99.8%) were purchased and used without further purification. A water purification system (Instrubal, Zener Power II) in the laboratory was used to produce the de-ionized water.

2.2. Synthesis of MIL-101(Cr)

In a typical procedure, 0.83 g (5 mmol) of terephthalic acid and 1.33 g (5 mmol) chromium chloride were ultrasonically mixed in 50 ml (2.78 mol) of de-ionized water. The equivalent of formic acid with respect to CrCl_3 was determined as 100 eq. Then the reaction mixture was heated up to 210 °C and held for 8 h under autogenous pressure. After cooling, the green powder precipitate was collected by centrifugation, washed twice with DMF and dried at 120 °C for 24 h.

2.3. Dielectric TiO_2 coating onto MIL-101(Cr) crystals

The synthesis process followed the procedure reported before with some amendment [10]. In brief, 0.5 g MIL-101(Cr) was first added into 100 ml solution containing 5 M HCl, 0.5 M TiCl_4 , and then the mixture was kept in an oven at 100 °C for 4 h for hydrolysis. The final product (referred to as $\text{TiO}_2/\text{MIL-101}$) was obtained by filtering and drying the slurry at 120 °C for 0.5 h.

2.4. Characterization

X-ray diffraction (XRD) patterns were obtained at room temperature by using a PANalytical X'Pert Pro powder diffractometer with Pixcel detector using Ni-filtered Cu-K α radiation (0.154 nm) in the range of $2\theta = 1-50^\circ$, and at a scanning rate of $0.1^\circ \cdot \text{s}^{-1}$. An Auriga Cobra Focused-Ion Beam Scanning Electron Microscope (FIB-SEM) was used to study the morphology of the obtained Cr-MOF samples. All the samples were mounted on a carbon tape and coated with gold prior to measurement. Fourier transform infrared (FTIR) spectra were scanned at 4 cm^{-1} resolution in the range of $500-4000 \text{ cm}^{-1}$ on a Perkin Elmer Spectrum 400 FT-IR/FT-NIR Spectrometer. Thermal stabilities of obtained samples were checked by a thermo-gravimetric analysis (TGA) instrument (Mettler, Toledo, TGA/SDTA 851°). Before measurements, all the samples were firstly washed with ethanol at 60 °C for 2 h, centrifuged off and rinsed using fresh ethanol one more time and dried. 10 mg of target sample was loaded into a pan and heated to 1000 °C at a rate of $10^\circ \text{C min}^{-1}$. The nitrogen flow was maintained at $10 \text{ ml} \cdot \text{min}^{-1}$. Surface area and pore characteristics measurements were carried out on an ASAP 2020 HD analyzer (Micromeritics) using N_2 , and the BET surface areas were obtained from the N_2 isotherms. Hydrogen adsorption isotherms at 77 K and pressure up to 1 bar were also measured on the ASAP 2020 instrument. All gas sorption isotherms were obtained using ultra-high purity grade (99.999%) gases. Considering that the as-prepared MOF samples may contain free carboxylic acid within the pores, before analysis, MOF samples (0.2–0.3 g) were first solvent-exchanged using ethanol, pre-treated in an oven and then outgassed in the analysis tube under vacuum (down to 10^{-7} bar) with heating up to 200 °C, which is sufficient to remove impurities without causing thermal decomposition or loss of framework crystallinity. The skeletal densities of the UiO-66(Zr) samples after ASAP tests were measured by a helium pycnometer (AccuPyc II 1340, Micromeritics), and average values were taken from three tests for each sample.

Nuclear Magnetic Resonance (NMR) spectra of the ortho-to-para hydrogen spin conversion were obtained with a Bruker AVANCE III HD 500 MHz (11.1 Tesla) standard bore spectrometer and triple channel broad band probe (TrigammaTM MAS probe). Ortho-hydrogen has a net magnetic moment that can be detected using NMR and

quantified by integrating the Fourier transformed Free Induction Decay (FID), while, para-hydrogen produces no net magnetic field, thus does not produce any NMR signal. This theory can be used to quantify the presence of para-hydrogen when an unknown sample is compared to a normal hydrogen sample [12].

3. Results and discussion

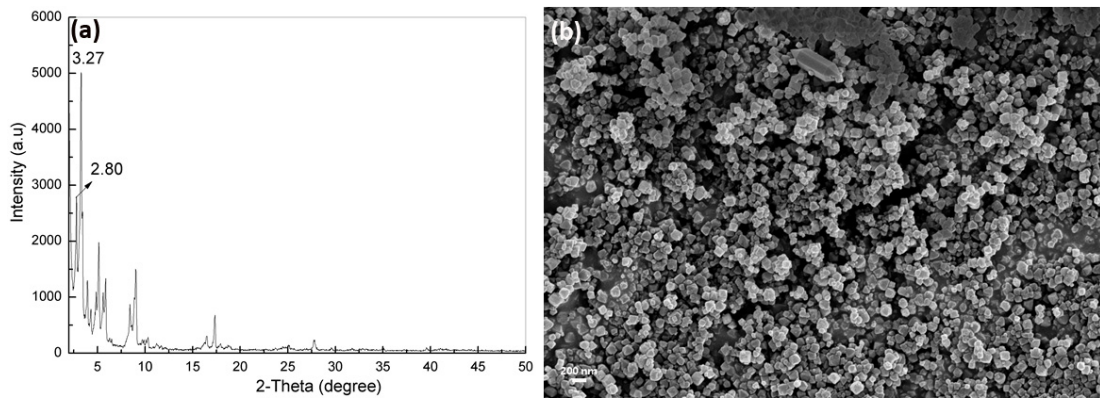


Fig. 2. (a) XRD pattern, and (b) SEM image of the synthesized MIL-101(Cr) sample

Two characteristic reflection signals in Fig. 2a positioned at $2\theta = 3.27$ and 2.8° confirmed the successful synthesis of MIL-101(Cr) when compared to the simulated XRD pattern [13]. The crystals morphologies in Fig. 2b show different irregular shapes. The synthesized MIL-101(Cr) crystals will be used as the conversion catalysts from ortho-hydrogen to para-hydrogen, and NMR will be used to identify the conversion process.

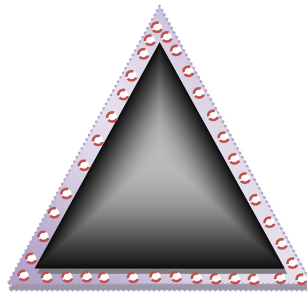


Fig. 3. Schematic illustration of dielectric TiO_2 coating onto MIL-101(Cr) crystal.

Fig. 3 shows the schematic illustration of dielectric TiO_2 coating onto MIL-101(Cr) crystal. The hybrid material will be characterized first and then used as the adsorbent materials in the hydrogen storage tank to prevent the re-establishment of the room temperature thermal equilibrium. The enhanced para-hydrogen storage is achieved by the charged solid surface and polarized hydrogen molecules caused by the field induced polarization of the dielectric material. This work is still ongoing and relevant results will be reported later.

4. Conclusion

In this study, the para-hydrogen is enriched from ultra-purity hydrogen using designed MOF-based hybrid composites with rich dielectric properties. The polarized hydrogen molecules caused by the field induced polarization of dielectric materials is responsible for the improved experimental observations.

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