Novel and Versatile Cobalt Azobenzene-Based Metal-Organic Framework as Hydrogen Adsorbent

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A novel URJC-3 material based on cobalt and 5,5'-(diazene-1,2-diyl)diisophthalate ligand, containing Lewis acid and basic sites, has been synthesized under solvothermal conditions. Compound URJC-3, with polyhedral morphology, crystallizes in the tetragonal and $P4_32_12$ space group, exhibiting a three-dimensional structure with small channels along a and b axes. This material was fully characterized, and its hydrogen adsorption properties were estimated for a wide range of temperatures (77–298 K) and pressures (1–170 bar). The hydrogen storage

capacity of URJC-3 is quite high in relation to its moderate surface area, which is probably due to the confinement effect of hydrogen molecules inside its reduced pores of 6 Å, which is close the ionic radii of hydrogen molecules. The storage capacity of this material is not only higher than that of active carbon and purified single-walled carbon nanotubes, but also surpasses the gravimetric hydrogen uptake of most MOF materials.

1. Introduction

Metal-organic framework materials (MOFs) have attracted increasing attention during the last years, particularly due to their interesting variety of architectures and topologies, which are defined by the abundant organic ligands, metals and crystallization conditions.^[1–4] Because of the high customize ability of these porous structures, they have been considered as potential candidates for a wide range of applications such as gas storage, heterogeneous catalysis, drug delivery and sensing, among others.^[5,6] Considering the high demand for efficient use of clean and renewable energy, and being hydrogen an attractive fossil fuel alternative owing to its high gravimetric energy density, the development of hydrogen storage materials has been strongly promoted.^[7–10] Among them, MOF materials are able to store hydrogen through physisorption mechanism, which presents many advantages in comparison with chemisorption in chemical hydrides, such as total reversibility and fast adsorption-desorption kinetics.^[11–13]

Inspired by these premises, a wide range of MOF materials has been rationally designed for hydrogen storage

applications.^[14–20] It is well known that the chemical nature of both, metal clusters and organic linkers, have a huge influence in the interactions between H_2 molecules and MOF structure.^[21,22] In our and other previous studies, it has been observed that cobalt-based MOFs show high affinity to hydrogen molecules, reaching higher isosteric heat of adsorption values than other isostructural frameworks based on different metals, maybe since cobalt could act as a Lewis acid site.^[23–28] Moreover, numerous works report that MOFs constructed by aromatic ligands use to show high internal surface areas, displaying significant hydrogen uptakes.^[7,21,29] Particularly, carboxylic linkers, which are easily deprotonated, are able to form MOF materials with different geometries constituted by multiple strong metal-oxygen coordination bonds that provide good thermal stability and rigidity to the framework.

In this regard, the synthesis of new cobalt-based materials using the multifunctional ligand, 5,5'-(diazene-1,2-diyl)diisophthalic acid (H_4ABTC) has been explored over the last years.^[30–37] The coordination chemistry of H_4ABTC is interesting since its four carboxylate groups can be partially or completely deprotonated in order to generate H_2ABTC^{2-} , $HABTC^{3-}$, and $ABTC^{4-}$ anions under different synthesis conditions that can coordinate with metal ions in multiple ways. Besides, the azo functionality is well-known as photochromic group that could reverse its geometrical isomerization between *cis* and *trans* states upon irradiation and other conditions, leading to the possibility of forming a series of MOF materials with interesting topologies and properties.^[38–40] In addition, the presence of azobenzene group from the ligand could contribute in improving the H_2 -MOF interaction as a result of the lone pair of electrons on the nitrogen atoms that could perform as Lewis base.^[41]

In this context, herein we report the solvothermal synthesis of a novel cobalt azobenzene-based metal-organic framework, named URJC-3. Moreover, the new structure has been eluci-

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dated and the bulk sample was characterized by different physico-chemical techniques. Finally, its hydrogen adsorption properties, as well as the affinity of the material to H_2 molecules has been estimated by means of the adsorption-desorption isotherms at different temperatures and pressures.

2. Results and Discussion

The crystalline structure of the new material was solved by the single crystal X-ray diffraction technique. Compound URJC-3 ($[\text{Co}_2(\text{ABTC})(\text{DMF})_3 \cdot 2\text{DMF}]_n$) crystallizes in the tetragonal system and $P4_32_1$ space group. The asymmetric unit is comprised of two cobalt ions, three coordinated dimethylformamide (DMF) molecules and one independent 5,5'-(diazene-1,2-diyl) diisophthalate ion ligand (Figure 1A). Co1 atom exhibits an

Figure 1. A) Asymmetric unit of URJC-3, B) Coordination environment of Co^{2+} ions and C) 3D view of URJC-3 MOF. Hydrogen atoms have been omitted for clarity.

almost ideal octahedral environment established by three O donor atoms set from three carboxylate groups pertaining to three different ligand molecules, and three coordinated DMF molecules. Co2 atom shows a distorted octahedral geometry due to the presence of two small bond angles O–Co–O with values of $60.51(14)^\circ$ and $61.21(15)^\circ$, where cobalt is coordinated twice to two oxygens from the same carboxylate group and twice to one oxygen from another carboxylate (Figure 1B). In according to the coordination modes of the organic linker ABTC^{4-} , one of them is coordinated with eight cobalt ions exhibiting a bridging bis-bidentate coordination mode, and the other organic linker connects six cobalt ions, for which four carboxylate groups are in chelating bidentate mode while the other four show a tridentate chelating bridging mode with

cobalt atoms. Such building units are repeated to form a three-dimensional (3-D) network, containing Lewis acid sites from Co ions and Lewis basic sites from azobenzene groups from the ligand, suitable not only for hydrogen adsorption but also for catalysis purposes. It also has coordinated DMF molecules pointing towards the interior of the cavities (Figure 1C), differentiating two different cavities of around 8.19 and 14.85 Å, without extracting carbon and oxygen radii. These cavities are occupied by highly disordered DMF molecules that were masked by the Olex2 mask tool (see experimental section).

In order to confirm the purity of the crystalline phase of the material, experimental powder X-ray diffraction (XRD) pattern was compared to the simulated pattern from the crystallographic data (Figure 2). Thus, it was observed that both diffractograms match very well in most of the reflections, confirming the exclusive presence of URJC-3 crystalline phase. Moreover, by scanning electron microscopy (SEM) (inset in Figure 2), the morphology and size of the crystals were determined, observing that it is constituted by only polyhedral crystals with average size of 100 μm (Figure S3 in the Supporting Information).

The thermal stability of the material was studied by thermogravimetric analysis (TGA) analysis (Figure S4). Two main weight loss steps were found, the first occurs in the temperature range of 40–150 $^\circ\text{C}$, that could correspond to the loss of water and possible DMF molecules filling the pores and some of them coordinated to the structure. The second weight loss is detected from roughly 275 $^\circ\text{C}$, which was associated to the decomposition of the organic ligand, leading to the subsequent structure collapse.

The textural properties of URJC-3 were measured by Ar adsorption-desorption analysis at 87 K (Figure S5A). For this purpose, URJC-3 sample was previously activated under high vacuum at $1 \cdot 10^{-6}$ mbar and 120 $^\circ\text{C}$ during 6 h. The isotherm revealed the microporosity of the new material since the sharp adsorption at very low relative pressure. However, the typical plateau after the edged adsorption at low pressure described for Type I isotherms is not observed in this case, having a progressive slope that indicates possible desorption species such as coordinated DMF. The resulting Brunauer, Emmett and Teller (BET) specific surface area was 171 m^2g^{-1} , and a pore volume of 0.076 cm^3g^{-1} . Besides, the pore size distribution (PSD) was also estimated using non-local Density Functional Theory (DFT) method, obtaining a bimodal narrow distribution at around 6 and 11 Å (Figure S5B), which matches with the before mentioned crystallographic information of this structure. The crystalline density of the new material was 1.51 g cm^{-3} (Table 1), regarding the results of the He pycnometry analysis.

Hydrogen adsorption measurements, at different conditions of pressure and temperature were carried out in order to

Table 1. Textural properties of URJC-3.

Surface area [m^2g^{-1}]	Pore volume [cm^3g^{-1}]	Skeletal density [g cm^{-3}]	Crystal density [g cm^{-3}]
171	0.076	1.7	1.51

Figure 2. XRD patterns of powder URJC-3 sample and simulated from its single-crystal data.

determine the hydrogen adsorption properties of the activated novel MOF. First, the hydrogen adsorption data at 77 K and up to 16 bar were recorded and depicted in Figure 3. There, a type I profile regarding the IUPAC was identified, which is roughly saturated at 16 bar with a gravimetric hydrogen excess uptake of about 3.50 wt%, which corresponds to a total H₂ storage capacity of 3.63 wt% (Table 2). The sharp adsorption observed at 1 bar and 77 K for excess and total data represents approximately 60% of the overall uptake defined by the

Figure 3. Hydrogen adsorption isotherms at 77 K. Left: gravimetric units, right: volumetric units.

Table 2. Excess and total gravimetric and volumetric H₂ adsorption capacity of URJC-3 at 77 K and 18 bar.

Gravimetric H ₂ adsorption capacity		Volumetric H ₂ adsorption capacity	
excess [wt %]	total [wt %]	excess [g L ⁻¹]	total [g L ⁻¹]
3.50	3.63	53.35	55.40

saturation reached at 16 bar and 77 K, which is the typical behaviour of microporous adsorbents. Nevertheless, the absolute H₂ amount adsorbed for URJC-3 is moderately higher than expected, according to its low surface area, as rationalized by Chahine rule on a variety of microporous materials.^[42] This drifting from the tendency of the rule could be related to the higher interaction due to the confinement effect of hydrogen molecules inside the pores of the MOF structure when is endowed with small sized pores in the range near ionic radii of hydrogen molecules, which is the case of the 6 Å pores of URJC-3. The storage capacity of this material is not only higher than that of active carbon and purified single-walled carbon nanotubes,^[43] but also surpasses the gravimetric hydrogen uptake reached by other MOF materials such as ZIF-8, MIL-100 (Fe) and MOF-74(Zn, Mg).^[44–47]

In terms of volumetric units, which are more significant for H₂ storage applications in light-duty vehicles, URJC-3 displays an excess uptake of 53.35 g L⁻¹, which is a value far higher than the volumetric hydrogen storage capacity of a compressed-tank at the same conditions of pressure and temperature, about 5.4 g L⁻¹. This high volumetric value is probably related to the low pore volume and high crystal density of the material compared to other opener structures.^[7] This result has been also observed for other MOF materials with reduced pore volume that have been used for small molecules recognition and separation.^[48]

Additionally, the data of H₂ adsorption–desorption isotherms collected at room temperature (298 K) and high pressure (170 bar) for URJC-3 are shown in Figure 4 and Table 3. In this case the difference between the excess and total adsorption capacity of the material is more pronounced than at 77 K, in which case the saturation is nearly reached.

These results were also compared with the experimental excess hydrogen adsorption uptake at room temperature (RT)

Figure 4. Hydrogen adsorption isotherms at 298 K. Left: gravimetric units, right: volumetric units.

Table 3. Excess and total gravimetric and volumetric H_2 adsorption capacity of URJC-3 at 298 K and 170 bar.

Gravimetric H_2 adsorption capacity		Volumetric H_2 adsorption capacity	
excess [wt %]	total [wt %]	excess [wt %]	total [wt %]
0.23	0.32	3.47	4.7

of the well-known MOF-5 and PCN-5 materials with BET surface areas of 2296 and 2095 $m^2 g^{-1}$, for which were reached 0.25 and 0.19 wt%, respectively, at high pressure,^[7] similar than the 0.23 wt% reached by URJC-3. The novel material shows a medium-moderate hydrogen adsorption capacity at ambient temperature regarding its low surface area, comparing to other more porous MOF materials. This fact could be related to different features that URJC-3 exhibits like its reduced pore size near hydrogen ionic radii that favors the confinement effect of H_2 molecules inside its cavities; and the chemical nature of the MOF scaffold (cobalt metal and azo groups), which promote the interaction with H_2 molecules.

Finally, with the purpose of studying the strength of H_2 -MOF interactions, the isosteric heat of adsorption profile for URJC-3 was estimated (Figure 5), using the Clausius-Clapeyron equation applied to the hydrogen adsorption data at near RT (273, 298 and 323 K). There, it can be shown that the isosteric heat of adsorption at low hydrogen loadings is around 8.4 $kJ mol^{-1}$, which is a rather high value among the average for MOF materials.

3. Conclusions

A novel versatile cobalt and azobenzene metal-organic framework, called URJC-3, containing Lewis acid and basic sites, has been synthesized and properly characterized by single and powder crystal X-ray diffraction, SEM, Ar adsorption at 87 K, TGA, and FT-IR. Compound URJC-3, with polyhedral morphology, crystallizes in the tetragonal and $P4_32_12$ space group, exhibiting a three-dimensional structure with small channels

Figure 5. Heat of adsorption plotted as a function of the volumetric amount of H_2 adsorbed at near RT.

along a and b axes. The reduced pore volume together with the nature of the metallic centers make this microporous material especially interesting for the recognition and adsorption of hydrogen molecules. Thus, the hydrogen storage capacity of URJC-3 was studied at different conditions of pressure and temperature, observing an interesting confinement effect of the H_2 molecules inside the cavities of the framework of around 6 and 11 Å. The excess hydrogen storage capacity of the novel MOF in gravimetric terms was 3.5 wt.% at 77 K and 20 bar, and 0.23 wt.% at 298 K and 170 bar, which are higher than the expected values considering its low surface area. Thus, in order to design the next generation of materials for on-board hydrogen storage at near RT, it is imperative to still improve the density of stored H_2 , maximizing the interactions of H_2 molecules with the MOF material.

Experimental Section

Synthesis of H_4 ABTC

The organic ligand 3,3',5,5'-azobenzene tetracarboxylic acid was prepared in according with the synthetic procedure described by Dhakshinamoorthy and colleagues,^[49] slightly modified by a further purification of the product by means of recrystallization in DMF (detailed synthesis procedure is in section S2 of the Supporting Information).

Synthesis of URJC-3

A mixture of 5,5'-(diazene-1,2-diyl)diisophthalic acid (0.01 mmol) and cobalt(II) nitrate hexahydrate (0.01 mmol) was dissolved in a mixture of N,N -dimethylformamide (5 mL) and some drops of nitric acid. The solution was then added to a 20 mL scintillation vial and placed in a preheated oven at 100 °C for 72 hours. After cooling down to RT, high quality crystals for single X-ray diffraction were obtained. Red crystals were isolated by decanting the mother liquid and washed with DMF. The resulting crystals were finally immersed in fresh DMF. Yield ca. 55% (based on linker). Fourier Transform Infrared (FT-IR) = 1656 (m), 1616 (s), 1552 (s), 1441 (s), 1377 (m), 1243 (m), 1105 (s), 920 (s), 776 (s) 715 (s) 681 (s) 514 (m) cm^{-1} . Anal.

Calc. for $C_{29.5}H_{37.5}Co_2N_{6.5}O_{12.5}$ (1): C, 40.58; H, 4.33; N, 10.23. Found: C, 44.23; H, 4.68; N, 11.37.

Materials and Methods

X-ray data collection of suitable single crystals of compound URJC-3 was performed at 100(2) K on a Bruker VENTURE area detector equipped with graphite monochromated Mo- $K\alpha$ radiation ($\lambda = 0.71073$ Å) by applying the ω -scan method. The data reduction was performed with the APEX2^[50] software and corrected for absorption using SADABS.^[51] Crystal structure was solved by direct methods using the SIR97 program^[52] and refined by full-matrix least-squares on F² including all reflections using anisotropic displacement parameters by means of the WINGX crystallographic package.^[53] All hydrogen atoms were included as fixed contributions riding on attached atoms with isotropic thermal displacement parameters 1.2 times or 1.5 times those of their parent atoms for the organic ligands. During the structure refinement, regions of electron density were identified as highly disordered DMF molecules. Attempts to model these electron densities as DMF were not successful due to the extent of the disorder. In the final structure model, the contribution of the electron density from 1.5 DMF molecules has been removed from the intensity data using the solvent mask tool in Olex2.^[54] The contribution from the 1.5 DMF molecule has been included in the empirical formula to give the correct calculated density, absorption coefficient and molecular weight. Details of the structure determination and refinement of compound is summarized in Table S1. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 1884280. Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, U.K. (Fax: +44-1223-335033; e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>). Powder X-ray Diffraction (XRD) analysis were carried out with a Philips X'PERT MPD equipment using Cu- $K\alpha$ monochromatic radiation (1.542 Å) with a 0.01 step, 10 s of accumulation time between steps and a non-proportional detector Xcelerator. Elemental analysis was carried out using an analyzer type ELEMENTAR VARIO EL III, equipped with a thermal conductivity detector. Ar adsorption-desorption measurements at 87 K were made in an AutoSorb equipment (Quantachrome Instruments). Specific surface area was calculated by the Brunauer-Emmett-Teller (BET) equation,^[55] while micropore volume and pore size distribution of materials were estimated by Non-Local Density Functional Theory (NL-DFT).^[56] Fourier Transform Infrared Spectra (FT-IR) were recorded in a FT-IR Varian Excalibur Series 3100 e UMA 600 spectrophotometer with a resolution up to 4 cm⁻¹. Thermogravimetric Analysis (TGA) was performed in a Mettler-Toledo DSC-TGA Star System device in air atmosphere, by heating samples at a rate of 1 °C/min. Skeletal density was determined through He pycnometry in an AccuPyc II 1340 apparatus. H₂ adsorption isotherms (99.999%) at 77 and 87 K were obtained on a Hiden Analytical Intelligent Gravimetric Analyser (IGA-003) equipped with an ultra-high vacuum system. The buoyancy correction was achieved after collecting He (99.99999%) adsorption-isotherms at 273 K. For H₂ adsorption-desorption isotherms at high pressure and room temperature (RT) conditions, a volumetric Quantachrome iSorbHP1 equipment was used, with an operation range of 0.06–200 bar. According to the National Institute of Standards and Technology reference values [NIST. Isothermal properties for hydrogen n.d.: <http://webbook.nist.gov/>], H₂ density was calculated by Helmholtz real-gas EOS.^[57] The adsorption isotherm model used for fitting the experimental adsorption data was the Virial 2 equation.^[54] The isosteric heat of hydrogen adsorption for material was calculated by the Clausius-

Clapeyron equation^[58] using data of H₂ adsorption isotherms at 273, 298 and 323 K (up to 170 bar).

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Conflict of Interest

The authors declare no conflict of interest.

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