



Stability and hydrogen adsorption of metal–organic frameworks prepared via different catalyst doping methods



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ABSTRACT

The stability of three metal–organic frameworks (MOFs), namely IRMOF-8, Cu-TDPAT, and Cu-BTC, was tested after incorporation of Pt. Stability was assessed with powder X-ray diffraction (PXRD), physical (N₂ at 77 K) and chemical (H₂ at 300 K) adsorption, and thermogravimetric analysis in H₂ and N₂. Introduction of Pt via wet precipitation led to MOF degradation during the H₂ reduction step. Addition of pre-reduced Pt supported on activated carbon (Pt/AC) to MOFs via physical mixing also led to structural degradation. However, addition of Pt/AC via a ‘pre-bridge’ (PB) technique led to high MOF stability, with the retention of surface area, porosity, crystallinity, and thermal stability. The catalytically active surface area was assessed by hydrogen adsorption, and demonstrated extension of the catalytically active surface area to the MOF surface. High hydrogen uptake correlated with MOF particle size, due to the connectivity between Pt/AC and MOF, and the interpenetration of Pt/AC into the MOF crystal.

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1. Introduction

The long-range structural order, high surface area (SA), adjustable pore size, and tunable functionality of metal–organic frameworks (MOFs) [1] have led to extensive study of these materials for gas storage and separation applications [2–5]. High surface area generally correlates with high cryogenic adsorption: MOF-177 [6], for example, with the highest SA to date (4500 m²/g [7]), has nominally met DOE gravimetric H₂ storage targets (7.5 wt% excess adsorption at 7 MPa, 77 K [8]), albeit at temperatures well below the DOE target temperature range. These same properties provide promise for application of MOFs in drug delivery [9], sensor development [10], and size-selective heterogeneous catalysis [11]. The stability of MOFs in terms of thermal and chemical stability has been tested previously [12], but to utilize MOFs as a catalyst support, the stability needs to be re-examined in the presence of the catalyst of interest.

A number of methods to incorporate catalytic transition metals into MOFs have been proposed and tested, including wet precipitation [13–16], incipient wetness [17], chemical vapor deposition (CVD) [18,19], and simple physical mixing (both with and without

introduction of a carbonized sugar to provide “bridges” between the presupported catalyst and MOF) [20]. However, to realize the aforementioned benefits of MOFs in catalytic applications, it is important that the catalytic doping method retains the MOF structural integrity, without introducing substantial defects, which may lead to irreproducibilities, poorly characterized structures, and long-term instability. It is well established that PXRD characterization of MOFs can be used to characterize structural degradation: peak splitting, changes in relative peak intensity, and/or the appearance/disappearance of peaks imply loss of structure [21,22]. Unfortunately, the structural stability of MOFs after catalyst addition has not been thoroughly examined. One possible exception is the synthesis and characterization of a Ru/MOF (MOF = Lanthanum-BTC, benzene tricarboxylate) catalyst for cyclohexene and benzene hydrogenation, where the catalyst Ru/MOF showed no obvious alteration in PXRD and had no loss in catalytic activity after five uses, with a turnover frequency (TOF) higher than 10,000 h⁻¹ [23]. In addition, a 0.5 wt% Pd/IRMOF-1 (Zn₄O(BDC)₃, BDC = 1,4-benzenedicarboxylate) catalyst used for liquid phase hydrogenation of ethyl cinnamate [24], showed a higher catalytic activity than a Pd/C catalyst, and the SA and micropore volumes upon Pd introduction was retained relative to the IRMOF-1 precursor (however, the textural properties of the IRMOF-1 were reduced by a factor of 3 relative to other reports [25]). Elsewhere, catalyst addition to MOFs generally led to reduced structural integrity, reduced surface area, or both. Platinum nanoparticles supported

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on IRMOF-1 introduced from the metal precursor PdCl₂ in liquid phase to catalyze C–C bond coupling reactions showed reasonable crystallinity in PXRD relative to undoped IRMOF-1, but N₂ 77 K adsorption isotherms showed a considerable reduction in SA and microporosity [16]. Despite initial reports (from multiple laboratories) that catalysts incorporated into MOFs could introduce a hydrogen dissociation source, initiate hydrogen spillover, and increase the operative hydrogen adsorption temperature to 300 K [15,19,20,22,26–33], these reports have been plagued by irreproducibilities that are perhaps associated with hierarchical “mesopore” structure and/or defects [28,34]. Close examination of the MOF characterization details after catalyst incorporation and H₂ exposure showed significant changes in PXRD peak intensity and broadening, with SA reduced by one-third [19]. Previous reports show similar alterations in PXRD and SA [20].

In this paper, we test the stability of select MOF supports after various doping techniques. Introduction of a Pt cationic precursor via a “wet chemistry” technique is compared to physical mixing via ball milling/grinding (used previously by Li and Yang [26]), and a hybrid “pre-bridge” technique [35,36], which introduces a supported Pt/AC (platinum on activated carbon) catalyst into the MOF synthesis slurry. Our primary focus was on (1) Zn-based IRMOF-8 (Zn₄O(NDC)₃, NDC = 2,6-naphthalenedicarboxylate) and (2) the Cu paddlewheel (Cu-PDW) based Cu-TDPAT ([Cu₃(TDPAT)(H₂O)₃], TDPAT = 2,4,6-tris(3,5-dicarboxylphenylamino)-1,3,5-triazine). IRMOF-8 has been reported to have very high ability to incorporate H₂ into its structure after catalytic doping [20], while the latter has amine functional groups, which could feasibly become positively charged to aid in traditional doping methods that require ion exchange. In select cases, we also consider (3) the Cu-BTC ([Cu₃(BTC)₂(H₂O)₃], BTC = 1,3,5-benzenetricarboxylate), as it has the same metal building unit as Cu-TDPAT (i.e., the Cu-PDW), but a purely carbon-based ligand like IRMOF-8. Structural stability is assessed with PXRD, low-pressure physical (N₂ at 77 K) and chemical (H₂ at 300 K) adsorption, and thermogravimetric analysis (TGA). Hydrogen adsorption is a common method to ascertain both metal dispersion and the catalytically active surface area, and also provides a screening tool for these materials for room temperature hydrogen adsorption capacity, although this specific topic will be addressed in a follow-up paper.

2. Experimental

2.1. Sample preparation

2.1.1. Synthesis of MOFs

The IRMOF-8 (abbreviated as **I**, see Fig. 1A) synthesis procedure utilized in this paper was based on a solvothermal method

reported by Yaghi et al. [37] and adapted for scale-up synthesis [22]. In brief, 0.63 g Zn(NO₃)₂·6H₂O and 0.15 g 2,6-H₂NDC were dissolved in 50 ml of DEF (Diethylformamide) solvent, and ultrasonicated for better ion dispersion. The solution was then heated to 368 K for 15 h to precipitate pale white fine crystalline powders ([Zn₄O(NDC)₃·(DEF)₆]). After filtration, the as-prepared sample was immediately outgassed and pretreated in argon flow (~30 sccm, standard cubic centimeter per minute) at 473 K for 5 h to remove residual solvent since the presence of DEF could cause permanent structural defects [21]. The yield of **I** based on limiting reactant H₂NDC was about 60%.

Similar solvothermal procedures were used for Cu-TDPAT (abbreviated as **T**, see Fig. 1B) synthesis [38]. Crystals of **T** were grown by a reaction of 0.68 mmol Cu(NO₃)₂·6H₂O, 0.05 mmol H₆-TDPAT in 2 ml DMA (Dimethylacetamide), 2 ml DMSO (Dimethyl sulfoxide), 0.2 ml H₂O and 0.9 ml HBF₄ at 358 K for three days. The blue polyhedron crystals ([Cu₃(TDPAT)(H₂O)₃]·10H₂O·5DMA) were collected and then washed with 10 ml DMA for three times. Methanol exchange was carried out every 1 h during daytime for one week for solvent exchange.

Crystals of Cu-BTC (abbreviated as **B**, see Fig. 1C) were grown by a microwave reaction [39] of 0.81 mmol Cu(NO₃)₂·6H₂O, 0.6 mmol H₃ BTC (1,3,5-benzenetricarboxylic acid) in 6 ml DMF (Dimethylformamide) at 413 K for 1 h. The blue crystals ([Cu₃(BTC)₂(H₂O)₃]) were collected and then washed with 10 ml DMF three times. Ethanol exchange was carried out every 1 h for one week.

2.1.2. Direct doping (DD) of Pt catalyst

IRMOF-8 (**I**) and Cu-TDPAT (**T**) were direct-doped (DD) with Pt by adopting techniques from Sabo et al. [17] to produce DD-**I** and DD-**T**, respectively. For DD-**I**, 100 mg of **I** was placed on a watch glass with a magnetic stirrer, and 10 mg of platinum acetylacetonate (Pt(acac)₂, Aldrich) in 1 ml DEF (Diethylformamide, TCI Chemicals) was added to the substrate to produce an expected 5 wt% Pt. The slurry was stirred and dried with argon flow for 2 h, outgassed in vacuum (<1 Pa) at room temperature overnight, preheated in a tube furnace at 353 K for 2 h in Ar purge gas, and then reduced in H₂ to 423 K for 1 h. DD-**T** was synthesized following a similar procedure with 200 mg of **T** and 20 mg of Pt(acac)₂ in 2 ml DEF. Pt/AC₁ was prepared in the same manner, using Maxsorb activated carbon (AC, Kansai Coke and Chemicals Co., Ltd., Japan; sample provided by the National Renewable Energy Laboratory, CO) as the substrate. Pt/AC₂ was prepared by adopting an ultrasound-assisted wet impregnation of chloroplatinic acid (H₂PtCl₆) described by Yang's group [31,40]. The 200 mg Maxsorb AC was dispersed in 50 ml acetone (EMD Millipore), and then stirred in a closed Erlenmeyer flask while 26 mg of H₂PtCl₆·6H₂O (STREM) in 4 ml of acetone was slowly added dropwise (~20 s/drop). After

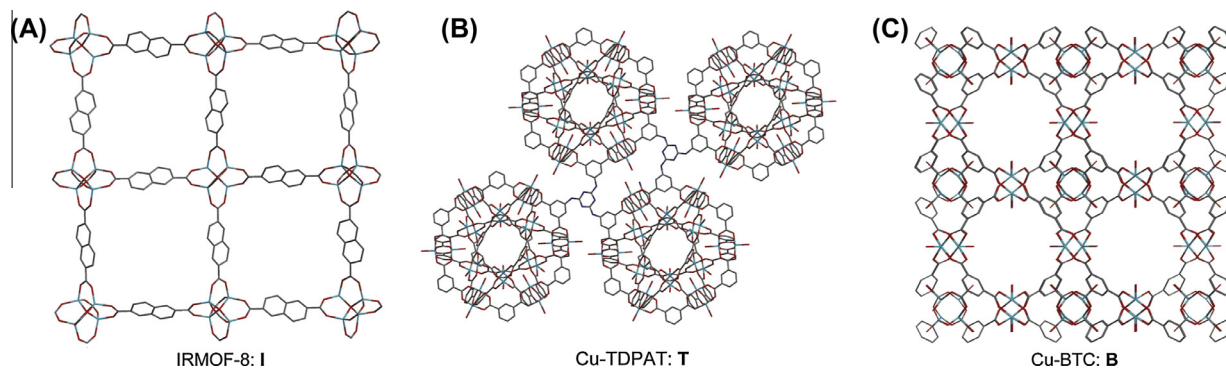


Fig. 1. Diagram of IRMOF-8 (**I**), Cu-TDPAT (**T**), and Cu-BTC (**B**), in which zinc (for **I**) and copper paddlewheel (for **T** and **B**) structure work as metal clusters, while the organic ligand (**I**: NDC, **T**: TDPAT, **B**: BTC) connects with metal cluster to form the long-range order MOF structure. TDPAT contains N in the center rings as well as 3 branches stretching from the center ring, similar to melamine (Gray: C, Red: O, Cyan: Cu or Zn, Blue: N). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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