Nanostructure and Hydrogen Spillover of Bridged Metal-organic Frameworks

The present study demonstrates that RT hydrogen uptake via bridged spillover is mainly governed by the imperfect lattice structure (including the structural defects) and pore network in real metal-organic framework (MOF) crystals. The hydrogen uptake can be further enhanced up to ~1.8 times (at 6.9 MPa) higher than the highest value reported regardless of the measured specific surface area of the MOF by tuning the synthesis factors. The special 3-D open pore network in the synthesized MOF crystal is related to the migration of atomic hydrogen and its presence facilitates the adsorption via spillover. X-ray diffraction and small-angle X-ray scattering are performed to study the various structures from the atomic scale to global scale. A relationship among the synthesis conditions, structural characteristics and hydrogen uptake via spillover in the bridged MOF as a conceptual breakthrough will also be proposed herein to provide an approach to optimizing the reversible RT hydrogen uptake.

Hydrogen storage is one of main challenges of the hydrogen economy and one of the bottlenecks to commercializing fuel-cell vehicles. New porous metal-organic frameworks (MOFs) have been identified as promising candidates for hydrogen storage.\(^1\) However, according to the U.S. Department of Energy (DOE) onboard criteria, the hydrogen uptake procedure must be reversible at ambient temperatures. Recently, Yang’s group used secondary spillover on the MOFs as a novel approach to significantly enhance their reversible RT hydrogen uptake up to 4 wt % at 10 MPa,\(^2\) a level which the currently available microporous materials cannot achieve via \(\text{H}_2\) physisorption under the same conditions.

In the hydrogen spillover process, the adsorption/desorption of spillover hydrogen atoms instead of \(\text{H}_2\) occurs in the MOF (as the secondary receptor) mixed with a small amount of a carbon-supported Pt catalyst (as the primary spillover source), which can dissociate hydrogen molecules.\(^3\) The dissociated atomic hydrogen migrates from the Pt surface to the carbon support (so-called primary spillover) and then moves to the MOF (secondary spillover). However, the mechanistic details of atomic hydrogen spillover are poorly understood. Currently, the understanding of the transport of spillover hydrogen atoms is limited to the surface diffusion processes both within the carbon support and within the high-capacity MOF receptor. There is a general lack of knowledge regarding the correlation of the hydrogen uptake via spillover to the structures, such as the pore network, specific surface area (SSA) and lattice defects.

Three different carbon-supported Pt catalysts were selected in our bridged IRMOF-8 system to quantitatively study the effect of both the Pt and carbon structures on the RT hydrogen uptake via bridged spillover. Anomalous small-angle X-ray scattering (ASAXS) with two synchrotron energies was employed to simultaneously resolve the structural characteristics of the Pt particle and carbon support. Prepared IRMOF-8 crystals with different lattice defects, SSA values and pore network structures were

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investigated here for the first time by SAXS and powder X-ray diffraction (XRD).

The IRMOF-8 crystals whose structures were to be characterized by XRD and N₂ sorption isotherm analysis were prepared. The synthesized IRMOF-8 crystals, which had a broad range of Brunauer-Emmet-Teller (BET) SSA values, were divided into three categories, denoted as M_SC1 (SSA: ~1400 m²/g; typical IRMOF-8), M_SC2 (SSA: ~900 m²/g; obtained by lowering the cooling rate) and M_SC3 (SSA: ~400 m²/g; obtained by an extended heating time with a scaled-up amount). The bridged IRMOF-8 samples were subsequently prepared including the use of commercial 5 wt% Pt supported on active carbon (Pt/AC). The hydrogen storage measurement for a selected bridged M_SC1 sample (denoted as INER-SWRI) was performed independently at the South West Research Institute (SWRI), USA, for a cross-check of our high-pressure thermal gravimetric analysis (TGA).

It can be seen in Fig. 1 that the hydrogen uptake of the bridged M_SC1 sample obtained by our regular TGA measurement at RT and 6.9 MPa was confirmed by its agreement with the data of the INER-SWRI sample. Moreover, the hydrogen uptakes of the bridged M_SC2 and 3 samples measured at RT and 6.9 MPa reached up to 4.2 wt%, which is much higher than that (~2.6 wt%) of the materials reported by Yang et al[2] under the same measurement conditions. Additionally, their corresponding equilibrium adsorption values were enhanced by up to 4.7 wt% at 6.9 MPa. It should be noted that the high RT hydrogen uptakes are not related to the measured SSA values of IRMOF-8 but can be attributed to differences in the structural defects (at the lattice scale) and the mesopore network of the real IRMOF-8 crystals.

The pore quality of the IRMOF-8 sample studied herein is very similar to that of the imperfect MOF-5 crystals reported previously,[4] which contain a partially collapsed framework. The amount of the produced structural defects in the lattice (i.e., the Zn-O species in the nanopores and lattice interpenetration as the minor phase) increases in order from M_SC1 to M_SC3, as revealed by the differences in peak splitting and relative peak intensities in the powder XRD pattern. These results consistently support the fact that the BET SSA value measured by the nitrogen sorption isotherm at 77 K is significantly reduced from ~1400 to ~400 m²/g (from M_SC1 to M_SC3) due to the different degrees of blockage of the lattice defects acting as a diffusion hindrance to nitrogen molecules. In the present study, the diffusion of the spillover H atoms is less limited in the collapsed framework structure than that of the H molecules.

Our SAXS study[5] shows that all of the prepared IRMOF-8 samples have a 3-D pore network formed by the aggregation of mesopores as well as micropores. The dense pore network of many branches displays the characteristics of self-similarity to some extent (fractal-like). The degrees of density and resultant branches of the pore network progressively increase from M_SC1 to M_SC3, as indicated by the increase in the slope associated with the power-law scattering in the low-Q region of the SAXS profiles (fractal dimension). The formation of the pore network by the aggregation of micropores occurs concurrently with the development of the lattice defects, as shown by the previously combined XRD and SAXS work.[4] It might be inferred that mesoscale (> 2 nm) pore channel networks distributed along the dense lattice defects (collapsed framework) have laterally narrow branches (down to the atomic hydrogen scale) that penetrate the boundaries and connect the isolated subgrain-like regions with high theoretically accessible SSA values.

The SAXS contributed purely from the pure Pt particles and carbon can be resolved from the ASAXS profiles of the carbon-supported catalysts. The radii of the Pt particles for commercial 5 wt% Pt/AC (SC) were determined to be ~27.7 nm and ~2.1 nm (bimodal size) by spherical form factor model fitting. The radii of the
Pt particles for commercial 10 wt % Pt/C (E-TEK) and 40 wt % Pt/C (JM), determined by SAXS analysis, were 1.6 nm and 2.4 nm, respectively. The carbon black (E-TEK, with a measured BET SSA of ~200 m$^2$/g) has a smooth surface. The active carbon (SC, with a measured BET SSA of ~1000 m$^2$/g) additionally consists of a dense branch (fractal-like) network of nanopore channels (~1.4 nm in width), which is evidenced by the power-law characteristics of the SAXS profile. This result suggests that the porous carbon support with high SSA has an open pore channel network, thereby providing more sites and effective pathways for the migration of spillover hydrogen atoms to the IRMOF-8 and hence leading to higher hydrogen uptake than the usual carbon black. The spillover mechanism and the associated various structures from the atomic scale to global scale is schematically illustrated in Fig. 2.

In conclusion, the optimization of the structures of the imperfect lattice and pore network can significantly facilitate the spillover and thus enhance the RT hydrogen uptake at moderate pressures, up to an amount of full coverage of hydrogen in the MOF (i.e., theoretical maximum storage), regardless of the total SSA value and micropore volume. Our results suggests that a further enhancement in RT hydrogen storage via bridged spillover not only depends on the development of new MOF materials but also on the control of the lattice defects and pore network structure associated with the MOF crystal, which can be optimized by synthesis conditions.

**Experimental Station**
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**Publications**

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