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## Light-Enhanced Acid Catalysis over a Metal-Organic Framework†

Caiyun Xu,<sup>‡a</sup> Keju Sun,<sup>‡b</sup> Yu-Xiao Zhou,<sup>a</sup> Xiao Ma,<sup>a</sup> and Hai-Long Jiang<sup>\*a</sup>Received 00th January 20xx,  
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**A Brønsted acid-functionalized metal-organic framework (MOF), MIL-101-SO<sub>3</sub>H, was prepared for acid-engaged esterification reactions. Strikingly, for the first time, the MOF exhibits significantly light-enhanced activity and possesses excellent activity and recyclability, with even higher activity than H<sub>2</sub>SO<sub>4</sub> under light irradiation.**

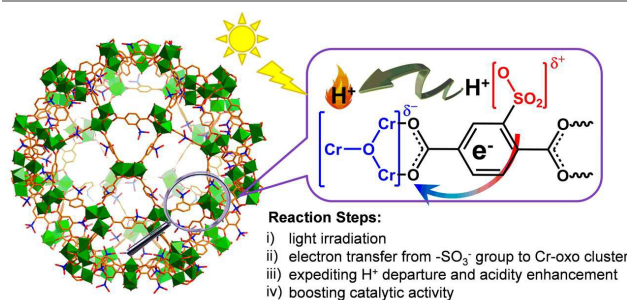
Catalysis is ubiquitous in nature during the development of the human society, of which catalyst plays a central role. Homogeneous Brønsted acids, such as H<sub>2</sub>SO<sub>4</sub>, are highly efficient and widely used in the production of important industrial chemicals. These traditional acid catalysts in liquid phase usually suffer from difficulty with respect to the separation from product mixtures. The principles of green chemistry stimulate the replacement of these acid catalysts with recyclable, separable solid Brønsted acids. Integration of strongly acidic functional group -SO<sub>3</sub>H onto different solid supports, such as metal oxides, carbon-based materials, *etc.*,<sup>1</sup> has been explored to develop solid Brønsted acid catalysts. Unfortunately, the common sulfonate functionalization based on concentrated H<sub>2</sub>SO<sub>4</sub> is hardly controlled over even distribution of -SO<sub>3</sub>H groups. Moreover, their activities are normally lower than those of homogeneous catalysts because of the lower degree of exposure of active sites to the reactants.

Metal-organic frameworks (MOFs) are crystalline porous solids with infinite network structures built from organic linkers and inorganic metal ions/clusters.<sup>2</sup> MOFs have been demonstrated to be promising functional materials in various

fields, especially in catalysis.<sup>3-5</sup> Given the highly tailorable and readily functionalized nature of MOFs, -SO<sub>3</sub>H group has been successfully grafted onto the frameworks of different MOFs,<sup>6</sup> such as UiO-66-SO<sub>3</sub>H, MIL-101-SO<sub>3</sub>H, which enables the Brønsted acid sites uniformly distributed throughout the MOF channels and thus easily accessible. The large specific surface area, well-ordered porous structure and high density of sulfonic acid group are beneficial to the diffusion and transport of substrates and products through MOF channels, sufficient exposure of the acid sites, making sulfonated MOFs ideal solid acid catalysts. Despite this, compared with traditional strong acid H<sub>2</sub>SO<sub>4</sub>, the protons of sulfonated MOFs are released in a relatively low extent and/or slow speed. Upon dissociation equilibrium, the acid strength hardly reaches a high value to give high reactivity.

To achieve a high acidic reactivity, it is necessary to develop effective solutions to expedite the departure of proton from sulfonic acid group and generate a high proton concentration for catalytic reaction. Many MOFs behave like semiconductors and can be excited under light irradiation to induce charge separation like ligand-to-metal electron transfer,<sup>7</sup> which might promote the departure of proton on the ligand and thus boost the acid-catalyzed reactions.

With the above considerations in mind, a sulfonic acid functionalized MOF, MIL-101-SO<sub>3</sub>H, was employed as a solid



**Scheme 1** Illustration of light-enhanced acid-catalytic reactions over MIL-101-SO<sub>3</sub>H, involving electron transfer from -SO<sub>3</sub><sup>-</sup> groups to Cr-oxo clusters that benefits release of protons from the MOF.

<sup>a</sup>Hefei National Laboratory for Physical Sciences at the Microscale, CAS Key Laboratory of Soft Matter Chemistry, Collaborative Innovation Center of Suzhou Nano Science and Technology, Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, P.R. China.

E-mail: [jianglab@ustc.edu.cn](mailto:jianglab@ustc.edu.cn)

Homepage: <http://staff.ustc.edu.cn/~jianglab/>

<sup>b</sup>Key Laboratory of Applied Chemistry, College of Environmental and Chemical Engineering, Yanshan University, Qinghuangdao, Hebei 066004, P.R. China.

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‡These authors contributed equally to this work.

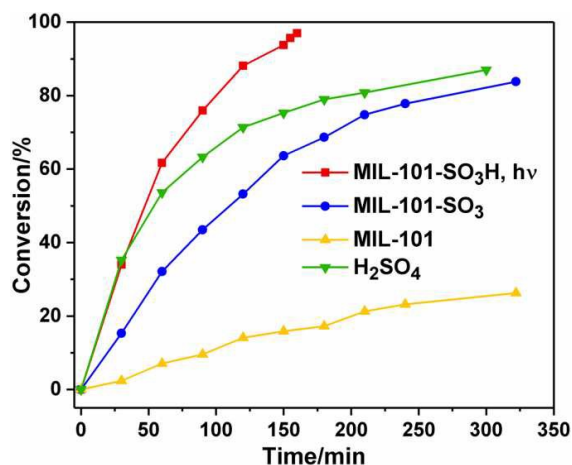
Brønsted acid catalyst to indicate considerable activity for esterification reactions and other Brønsted acid-catalyzed organic reactions. Strikingly, upon light irradiation, MIL-101-SO<sub>3</sub>H exhibits significantly enhanced activity, even higher than H<sub>2</sub>SO<sub>4</sub>. Moreover, the MIL-101-SO<sub>3</sub>H catalyst is readily recovered and recyclable. To our knowledge, this is not only the first work on light-enhanced MOF acid activity but also an unprecedented report on the higher activity of MOF-based acid catalysts than inorganic strong acid. Theoretical calculations suggest the charge separation in the MOF creates an electron withdrawing effect from -SO<sub>3</sub>H group, which boosts the proton liberation and thus increases the activity, upon photoexcitation (Scheme 1).

The representative MOF, MIL-101-SO<sub>3</sub>H (ideally formulated Cr<sub>3</sub>(H<sub>2</sub>O)<sub>3</sub>O(BDC-SO<sub>3</sub>H)<sub>2</sub>(BDC-SO<sub>3</sub>), BDC = 1,4-benzenedicarboxylic acid), was readily obtained via a solvothermal reaction followed by an acid exchange process.<sup>6c,d</sup> MIL-101-SO<sub>3</sub>H features a 3D MTN-type zeolitic structure with two types of mesoporous cages, in which the sulfonic acid groups are suspended on the cage walls (Scheme 1). The MOF possesses a high BET surface area of 1569 m<sup>2</sup>/g based on N<sub>2</sub> sorption at 77 K (Fig. S1, ESI<sup>†</sup>). The pore size distribution analysis manifests the presence of two types of cages in MIL-101-SO<sub>3</sub>H (Fig. S1, ESI<sup>†</sup>, inset), in consistent with that mentioned above. Moreover, the MIL-101-SO<sub>3</sub>H is able to absorb UV and visible light based on its UV-Vis spectrum (Fig. S2, ESI<sup>†</sup>).

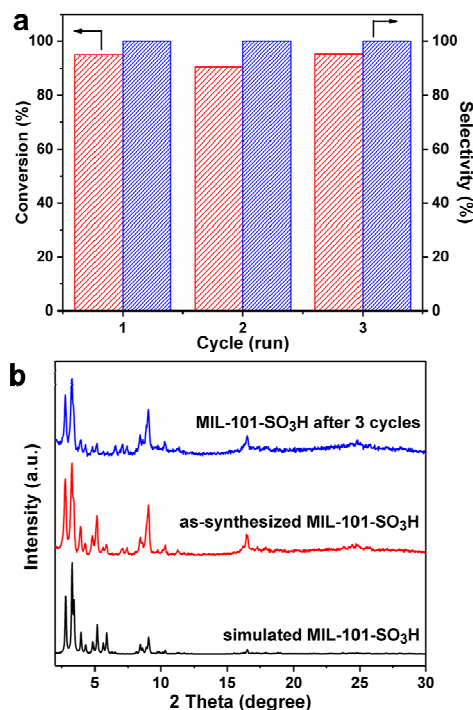
To explore the activity of MIL-101-SO<sub>3</sub>H, the esterification reaction between benzyl alcohol and acetic acid, was first chosen as a model reaction (Fig. 1, Table S1, ESI<sup>†</sup>). The reaction starting materials (benzyl alcohol and acetic acid in a 1:4 molar ratio) were heated to the desired temperature 80 °C in a reactor while being continuously stirred. With MIL-101-SO<sub>3</sub>H as a catalyst, it was able to reach 83.8% conversion with 100% selectivity in 322 min. The concentration of Brønsted acid sites in MIL-101-SO<sub>3</sub>H was estimated to be 1.75 mmol/g

by acid-base titration after stirring overnight for the MIL-101-SO<sub>3</sub>H suspension solution. With this information in hands, classical inorganic acid H<sub>2</sub>SO<sub>4</sub> with the same amount of catalytic sites as that in MIL-101-SO<sub>3</sub>H was employed in control experiment. As expected, the homogeneous catalyst with strong Brønsted acidity possesses a much higher initial rate than MIL-101-SO<sub>3</sub>H, possibly due to the less dissociation of -SO<sub>3</sub>H and lower concentration of H<sup>+</sup> ion in the latter. Unexpectedly, light irradiation can greatly boost the catalytic process over MIL-101-SO<sub>3</sub>H and the light-assisted conversion reached 97% in 160 min, unbelievably, which is even higher than that of H<sub>2</sub>SO<sub>4</sub>. The superior activity of the MOF catalyst to H<sub>2</sub>SO<sub>4</sub> in the later stage may be due to the enrichment effect of MIL-101-SO<sub>3</sub>H for reactants. In addition, MIL-101 with equivalent amount of Cr as a control was also conducted the esterification reaction. The activity of MIL-101 in Fig. 1 demonstrates that the Lewis acid sites in MOF also contribute to the reaction to a certain degree, while no similar light-enhanced phenomenon in MIL-101 can be observed (Fig. S3, ESI<sup>†</sup>). Apparently, light irradiation presents a significant effect on the reactivity of MIL-101-SO<sub>3</sub>H. Moreover, Lewis acid sites and the enrichment effect in MOF should also promote the process. As far as we know, there has been no report on a higher Brønsted acidic activity of MOF-based catalysts than H<sub>2</sub>SO<sub>4</sub> thus far, although the superacidity was reported in sulfated MOF most recently.<sup>8</sup>

It is also interesting to note that MIL-101-SO<sub>3</sub>H showed very good recyclability. As shown in Fig. 2a, the catalytic activity



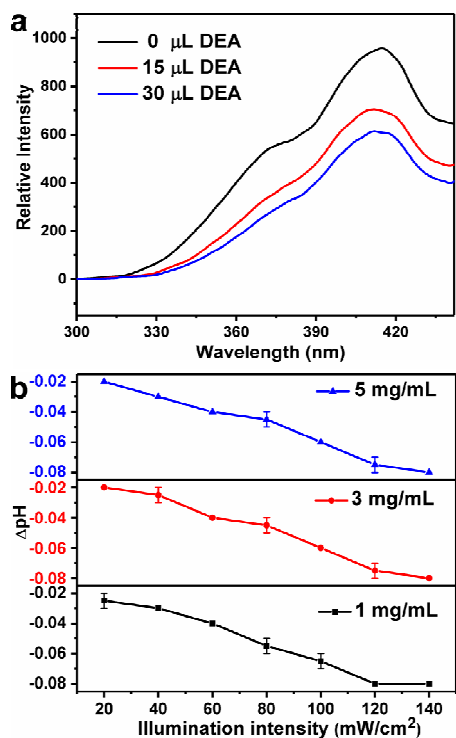
**Fig. 1** Time courses of the esterification reaction over various catalysts in the presence or absence of light irradiation. Reaction conditions: 10 mmol of benzyl alcohol, 40 mmol acetic acid, 80 °C in a reactor, hv = light irradiation with a 300 W Xeon lamp.



**Fig. 2** (a) Recycling tests for MIL-101-SO<sub>3</sub>H catalyst toward the esterification reaction under light irradiation; (b) powder XRD patterns for MIL-101-SO<sub>3</sub>H before and after three runs of catalysis.

remains very well during three consecutive runs for the esterification reaction between benzyl alcohol and acetic acid. All three runs of time-conversion plots are almost identical (Fig. S4, ESI<sup>†</sup>). Further evidence in support of the catalyst stability was obtained by the well retained powder XRD profiles before and after 3 runs of catalytic reaction (Fig. 2b).

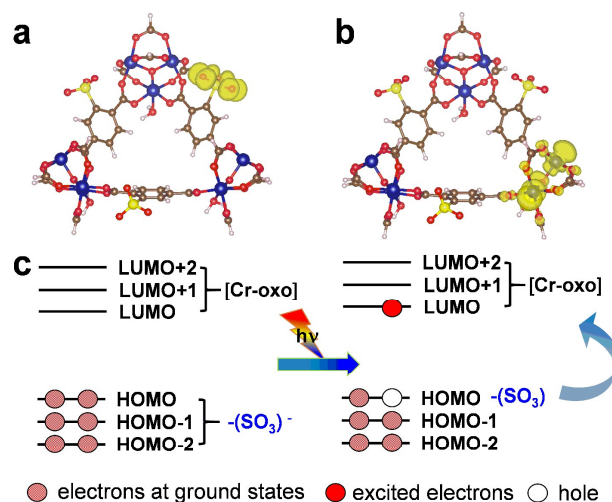
Encouraged by the excellent catalytic activity and recyclability of MIL-101-SO<sub>3</sub>H under light irradiation, the generality of the photo-induced activity enhancement has further been investigated in two other kinds of esterification reactions, e.g., cyclohexanol with acetic acid (Fig. S5, ESI<sup>†</sup> and Table S2, ESI<sup>†</sup>) and benzyl alcohol with propionic acid (Fig. S6, Table S3, ESI<sup>†</sup>), respectively. The time courses for both esterification reactions have unambiguously shown the light-enhanced activity, both of which are superior to those of H<sub>2</sub>SO<sub>4</sub>. In addition, different types of nucleophiles, such as aniline and tetrahydropyrrole, employed for ring-opening with styrene oxide gave absolute regioselectivity and further demonstrated the boosted activity by light irradiation (Table S4, ESI<sup>†</sup>). Moreover, Beckmann rearrangement (Table S5, ESI<sup>†</sup>), acetalization of aldehyde with diol (Table S6, ESI<sup>†</sup>) and transfer hydrogenation of imines (Table S7, ESI<sup>†</sup>) have been attempted. Delightedly, the results clearly show that all the reactions can be greatly boosted under light irradiation and exhibit higher activity over MIL-101-SO<sub>3</sub>H than the homogeneous H<sub>2</sub>SO<sub>4</sub> with the same amount of active sites (Table S5-S7, ESI<sup>†</sup>).



**Fig. 3** (a) Fluorescence emission spectra ( $\lambda_{\text{ex}} = 232$  nm) of MIL-101-SO<sub>3</sub>H in CH<sub>3</sub>OH in the absence or presence of different contents of the quencher DEA; (b) pH change versus light intensity for the suspension solution with different concentrations of MIL-101-SO<sub>3</sub>H. The curve drawn is to guide the eye and not a fit to the data.

It is highly desired to understand the reason behind the activity enhancement under light irradiation. The fluorescence emission at 300-440 nm of MIL-101-SO<sub>3</sub>H is quenched efficiently by electron-donating molecule N, N-diethylaniline (DEA) in solution (Fig. 3a), suggesting that MIL-101-SO<sub>3</sub>H can be an excellent photo-excited electron acceptor. Thus, it is assumed that MIL-101-SO<sub>3</sub>H can be excited under light irradiation to induce charge separation like ligand-to-metal electron transfer, similar to many MOF photocatalysts.<sup>7</sup> Upon *e-h* separation, the holes left on the -SO<sub>3</sub><sup>-</sup> group facilitate the proton liberation and thus increase acidity. In view of this, MIL-101-SO<sub>3</sub>H is assumed to exhibit a light-induced proton liberation and acidity enhancement. To further verify this hypothesis, the pH changes ( $\Delta\text{pH} = -\log\left(\frac{[\text{H}^+]_{\text{eq2}}}{[\text{H}^+]_{\text{eq1}}}\right)$ , see ESI<sup>†</sup>) of MIL-101-SO<sub>3</sub>H suspension in aqueous solution with various concentrations under different light intensities were investigated (Fig. 3b). The  $\text{pH}_{\text{eq1}}$  value decreases gradually along with increased concentration of MIL-101-SO<sub>3</sub>H. In contrast, with the light intensity increasing from 20 to 140 mW/cm<sup>2</sup>, the  $\Delta\text{pH}$  changes exhibit a similar trend regardless of catalyst concentration in the solution (Fig. 3b), indicating it is the light intensity that leads to the pH change in the solution involving MIL-101-SO<sub>3</sub>H. This result offers the evidence that the photo-assisted acidity enhancement of the MOF catalyst is attributed to the charge separation in MOF upon light irradiation.

To further clarify the inherent mechanism for the exciting phenomenon observed here, theoretical calculations have been conducted to investigate the orbital energy levels involved. A representative and typical ring-like building unit in MIL-101-SO<sub>3</sub>H structure, composed by three Cr-oxo clusters and three BDC-SO<sub>3</sub><sup>-</sup>/SO<sub>3</sub>H ligands was selected as a calculation model (Fig. S7, ESI<sup>†</sup>). Reasonably, -SO<sub>3</sub><sup>-</sup> and -SO<sub>3</sub>H should be present together in the model structure, due to the partial



**Fig. 4** (a) The HOMO is dominated by the -SO<sub>3</sub><sup>-</sup> groups and (b) the LUMO is dominated by the Cr-oxo clusters; (c) the calculated HOMOs and LUMOs for MIL-101-SO<sub>3</sub>H and proposed electron transfer upon photoexcitation, based on complete dissociation model of proton from the sulfonic acid group.

dissociation of  $-\text{SO}_3\text{H}$  in reaction solution. Therefore, two extreme structural models including complete dissociation (three  $-\text{SO}_3^-$ , Fig. 4 and Fig. S7a, ESI<sup>†</sup>) and initial dissociation (two  $-\text{SO}_3\text{H}$  and one  $-\text{SO}_3^-$ , Fig. S7b, ESI<sup>†</sup>) were built and calculated to investigate the contribution of orbital energy levels. Based on the calculated results of the both models, the HOMO (the highest occupied molecular orbital) is dominated by the  $-\text{SO}_3^-$  group while the LUMO (the lowest unoccupied molecular orbital) is dominated by the Cr-oxo clusters (Fig. 4; Fig. S8 and S9, ESI<sup>†</sup>). The release of one proton ( $\text{H}^+$ ) leaves one negative charge localized at the  $-\text{SO}_3^-$ , making the orbital energy level of  $-\text{SO}_3^-$  approximate to the HOMO. Thus, the electrons in the  $-\text{SO}_3^-$  can be excited to the LUMO if sufficient energy is provided by light. Based on the above results, we may assume that, upon exposing MIL-101- $\text{SO}_3\text{H}$  to light, the electrons at ground states of  $-\text{SO}_3^-$  are excited to the LUMO and the holes are left on the  $-\text{SO}_3^-$  to form  $-\text{SO}_3$  (Fig. 4c), the negative charge being no longer localized on it which is beneficial to the release of proton. This result is somewhat like the classical electron withdrawing effect of many groups, leading to the proton liberation and acidity increase, which would be maintained by continuous light irradiation.

In summary, a sulfonic acid group modified MOF, MIL-101- $\text{SO}_3\text{H}$ , behaves as a solid Brønsted acid catalyst toward various acid-catalyzed reactions. Particularly, we have demonstrated the activity is dramatically enhanced, which exhibits even higher activity than that of traditional strong acid  $\text{H}_2\text{SO}_4$ , under light irradiation. As far as we know, this is not only the first report on boosting acidity and acid-related reactivity over MOFs by light irradiation, but also the first work on the higher Brønsted acid activity of MOF-based materials than inorganic strong acids. The superb activity should be attributed to the Lewis acidity, substrate enrichment in MOF pores and improved proton liberation by light-induced electron transfer as well as the protons gathering inside the MOF cages, thus greatly boosting the acid-engaged reactions. The exciting results reported herein would pave the way to the development of light-enhanced MOF catalysis in many industrial processes.

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## Conflicts of interest

There are no conflicts to declare.

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