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Light-enhanced acid catalysis over a metal–organic framework†

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A Brønsted acid-functionalized metal–organic framework (MOF), MIL-101-SO_3H, 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_2SO_4 under light irradiation.

Catalysis is ubiquitous in nature during the development of the human society, of which the catalyst plays a central role. Homogeneous Brønsted acids, such as H_2SO_4, are highly efficient and widely used in the production of important industrial chemicals. These traditional acid catalysts in the 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. The integration of the strongly acidic functional group $-SO_3H$ onto different solid supports, such as metal oxides, carbon-based materials, *etc.*,[1] has been explored to develop solid Brønsted acid catalysts. Unfortunately, the common sulfonate functionalization based on concentrated H_2SO_4 is hardly controlled over even the distribution of $-SO_3H$ 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.[2] MOFs have been demonstrated to be promising functional materials in various fields, especially in catalysis.[3–5] Given the highly tailorable and readily functionalized nature of MOFs, the $-SO_3H$ group has been successfully grafted onto the frameworks of different MOFs,[6] such as UiO-66-SO_3H and MIL-101-SO_3H, which enables the Brønsted acid sites to uniformly distribute throughout the MOF channels and thus they are easily accessible. The large specific surface area, well-ordered porous structure and high density of the sulfonic acid group are beneficial for the diffusion and transport of substrates and products through MOF channels and sufficient exposure of the acid sites, making sulfonated MOFs ideal solid acid catalysts. Despite this, compared with traditional strong acid H_2SO_4, the protons of sulfonated MOFs are released in a relatively low extent and/or slow speed. At 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 the sulfonic acid group and generate a high proton concentration for the catalytic reaction. Many MOFs behave like semiconductors and can be excited under light irradiation to induce charge separation like ligand-to-metal electron transfer,[7] 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_3H, was employed as a solid Brønsted acid catalyst to indicate considerable activity for esterification reactions and other Brønsted acid-catalyzed organic reactions. Strikingly, upon light irradiation, MIL-101-SO_3H exhibits significantly enhanced activity, even higher than H_2SO_4. Moreover, the MIL-101-SO_3H 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 acids. Theoretical calculations suggest the charge separation in the MOF creates an electron withdrawing effect from the $-SO_3H$ group, which boosts the proton liberation and thus increases the activity, upon photoexcitation (Scheme 1).

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† Electronic supplementary information (ESI) available: Materials and instrumentation, synthetic procedures, experimental details, supplemental figures, methods and results of theoretical calculations. See DOI: 10.1039/c8cc00130h

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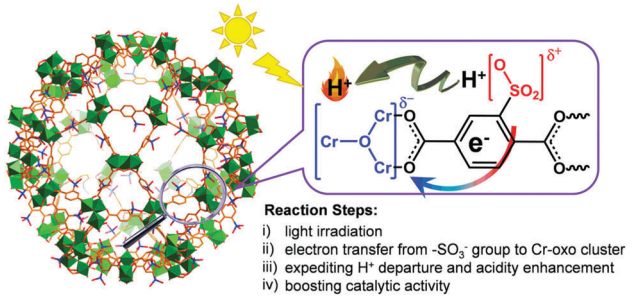

Scheme 1 Illustration of light-enhanced acid-catalytic reactions over MIL-101-SO_3H, involving electron transfer from $-SO_3^-$ groups to Cr–oxo clusters that benefits the release of protons from the MOF.

The representative MOF, MIL-101-SO_3H (ideally formulated as $Cr_3(H_2O)_3O(BDC\text{-}SO_3H)_2(BDC\text{-}SO_3)$, BDC = 1,4-benzenedicarboxylic acid), was facilely obtained *via* a solvothermal reaction followed by an acid exchange process.[6c,d] MIL-101-SO_3H 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 $m^2\ g^{-1}$ based on N_2 sorption at 77 K (Fig. S1, ESI†). Pore size distribution analysis manifests the presence of two types of cages in MIL-101-SO_3H (Fig. S1, ESI,† inset), consistent with that mentioned above. Moreover, MIL-101-SO_3H is able to absorb UV and visible light based on its UV-Vis spectrum (Fig. S2, ESI†).

To explore the activity of MIL-101-SO_3H, the esterification reaction between benzyl alcohol and acetic acid was first chosen as a model reaction (Fig. 1 and Table S1, ESI†). The reaction starting materials (benzyl alcohol and acetic acid in a 1 : 4 molar ratio) were heated to the desired temperature of 80 °C in a reactor while being continuously stirred. With MIL-101-SO_3H 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_3H was estimated to be 1.75 mmol g^{-1} *via* acid–base titration after stirring overnight the MIL-101-SO_3H suspension solution. With this information in hand, classical inorganic acid H_2SO_4 with the same amount of catalytic sites as that in MIL-101-SO_3H was employed in the control experiment. As expected, the homogeneous catalyst with strong Brønsted acidity possesses a much higher initial rate than MIL-101-SO_3H, possibly due to the less dissociation of $-SO_3H$ and lower concentration of H^+ ions in the latter. Unexpectedly, light irradiation can greatly boost the catalytic process over MIL-101-SO_3H and the light-assisted conversion reached 97% in 160 min, unbelievably, which is even higher than that of H_2SO_4. The superior activity of the MOF catalyst to H_2SO_4 in the later stage may be due to the enrichment effect of MIL-101-SO_3H on reactants. In addition, MIL-101 with an equivalent amount of Cr as a control was also subjected to the esterification reaction. The activity of MIL-101 in Fig. 1 demonstrates that the Lewis acid sites in the 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†). Apparently, light irradiation presents a significant effect on the reactivity of MIL-101-SO_3H. Moreover, Lewis acid sites and the enrichment effect on 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_2SO_4 thus far, although the superacidity was reported in a sulfated MOF most recently.[8]

It is also interesting to note that MIL-101-SO_3H showed very good recyclability. As shown in Fig. 2a, the catalytic activity remains very well during three consecutive runs for the esterification reaction between benzyl alcohol and acetic acid.

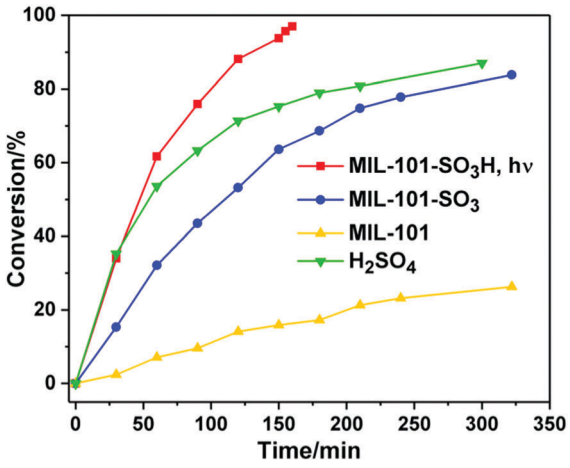

Fig. 1 Time courses of the esterification reaction over various catalysts in the presence or absence of light irradiation. Reaction conditions: 10 mmol of benzyl alcohol, 40 mmol of acetic acid, 80 °C in a reactor, $h\nu$ = light irradiation with a 300 W Xeon lamp.

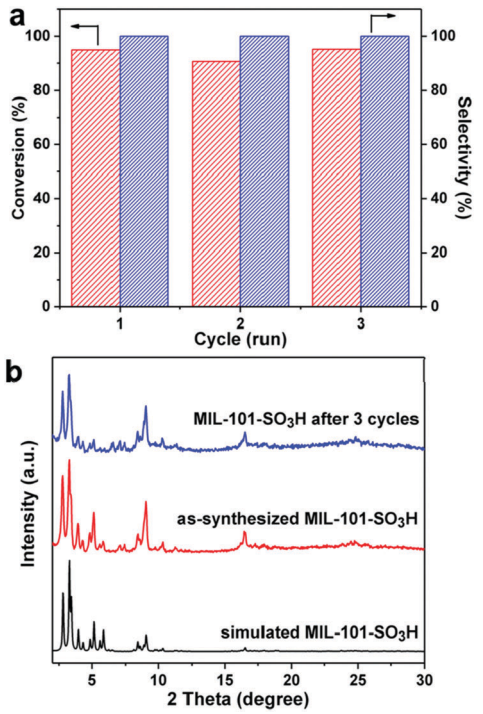

Fig. 2 (a) Recycling tests for the MIL-101-SO_3H catalyst toward the esterification reaction under light irradiation and (b) powder XRD patterns for MIL-101-SO_3H before and after three runs of catalysis.

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All three runs of time–conversion plots are almost identical (Fig. S4, ESI†). Further evidence in support of the catalyst stability was obtained from the well-retained powder XRD profiles before and after 3 runs of the catalytic reaction (Fig. 2b).

Encouraged by the excellent catalytic activity and recyclability of MIL-101-SO_3H 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 and Table S2, ESI†) and benzyl alcohol with propionic acid (Fig. S6 and Table S3, ESI†), respectively. The time courses for both esterification reactions have unambiguously shown the light-enhanced activity, both of which are superior to those of H_2SO_4. 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†). Moreover, Beckmann rearrangement (Table S5, ESI†), acetalization of aldehyde with diol (Table S6, ESI†) and transfer hydrogenation of imines (Table S7, ESI†) 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_3H than the homogeneous H_2SO_4 with the same amount of active sites (Tables S5–S7, ESI†).

It is highly desirable to understand the reason behind the activity enhancement under light irradiation. The fluorescence emission at 300–440 nm of MIL-101-SO_3H is quenched efficiently by the electron-donating molecule *N*,*N*-diethylaniline (DEA) in solution (Fig. 3a), suggesting that MIL-101-SO_3H can be an excellent photo-excited electron acceptor. Thus, it is assumed that MIL-101-SO_3H can be excited under light irradiation to induce charge separation like ligand-to-metal electron transfer, similar to many MOF photocatalysts.[7] Upon *e*–*h* separation, the holes left on the $-SO_3^-$ group facilitate the proton liberation and thus increase the acidity. In view of this, MIL-101-SO_3H is assumed to exhibit a light-induced proton liberation and acidity enhancement. To further verify this hypothesis, the pH changes ($\Delta pH = -\log([H^+]_{eq2}/[H^+]_{eq1})$, see ESI†) of MIL-101-$SO_3H$ suspension in aqueous solution with various concentrations under different light intensities were investigated (Fig. 3b). The pH_{eq1} value decreases gradually along with the increased concentration of MIL-101-SO_3H. In contrast, with the light intensity increasing from 20 to 140 mW cm^{-2}, the ΔpH changes exhibit a similar trend regardless of the catalyst concentration in the solution (Fig. 3b), indicating that it is the light intensity that leads to the pH change in the solution involving MIL-101-SO_3H. This result offers the evidence that the photo-assisted acidity enhancement of the MOF catalyst is attributed to the charge separation in the MOF upon light irradiation.

To further clarify the inherent mechanism of 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 the MIL-101-SO_3H structure, composed of three Cr–oxo clusters and three BDC-SO_3^-/SO_3H ligands, was selected as a calculation model (Fig. S7, ESI†). Reasonably, $-SO_3^-$ and $-SO_3H$ should be present together in the model structure, due to the partial dissociation of $-SO_3H$ in the reaction solution. Therefore, two extreme structural models including complete dissociation (three $-SO_3^-$, Fig. 4 and Fig. S7a, ESI†) and initial dissociation (two $-SO_3H$ and one $-SO_3^-$, Fig. S7b, ESI†) 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 $-SO_3^-$ group while the LUMO (the lowest unoccupied molecular orbital) is dominated by the Cr–oxo clusters (Fig. 4 and Fig. S8, S9, ESI†). The release of one proton (H^+) leaves one negative charge localized at the $-SO_3^-$, making the orbital energy level of $-SO_3^-$ approximate to the HOMO. Thus, the electrons in the $-SO_3^-$ 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-SO_3H to light, the electrons at ground states of $-SO_3^-$ are excited to the LUMO and the holes are left on the $-SO_3^-$ to form $-SO_3$ (Fig. 4c), the negative charge being no longer localized on it, which is beneficial to the release of protons. 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-SO_3H, behaves as a solid Brønsted acid catalyst toward various acid-catalyzed reactions. Particularly, we have demonstrated

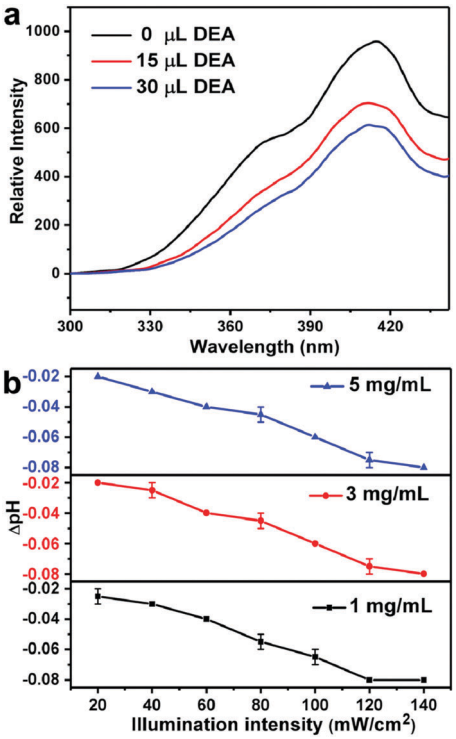

Fig. 3 (a) Fluorescence emission spectra (λ_{ex} = 232 nm) of MIL-101-SO_3H in CH_3OH in the absence or presence of different contents of the quencher DEA and (b) pH change *versus* light intensity for the suspension solution with different concentrations of MIL-101-SO_3H. The curve drawn is to guide the eye and not a fit to the data.

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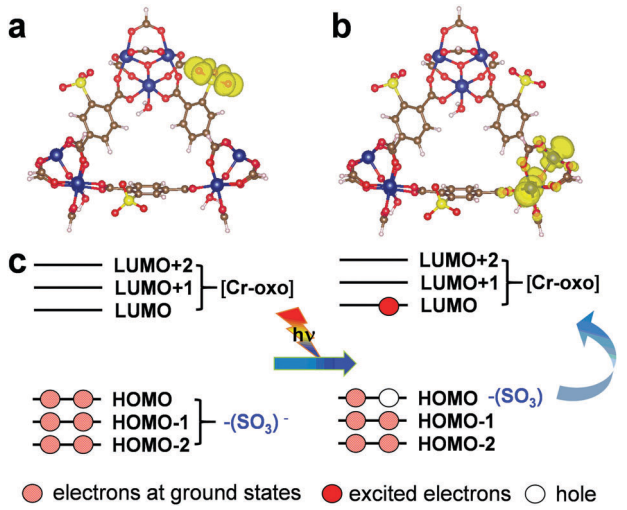

Fig. 4 (a) The HOMO is dominated by the $-SO_3^-$ groups and (b) the LUMO is dominated by the Cr–oxo clusters; (c) the calculated HOMOs and LUMOs for MIL-101-SO_3H and the proposed electron transfer upon photoexcitation, based on the complete dissociation model of protons from the sulfonic acid group.

that its activity is dramatically enhanced, which exhibits even higher activity than that of traditional strong acid H_2SO_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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